Reading Guide for “Isotope Effects in Arene C-H Bond Activation by [(C5Me5)Rh(PMe3)]” Jones, W. D.; Feher, F. J. *JACS*, **1986**, *108*, 4814. **DOI:** 10.1021/ja00276a019

**Part 1: understanding zero point energies**

1. In Newtonian mechanics and in the analysis of molecular vibrations in IR/Raman spectroscopy, the reduced mass, , allows the 2-body problem to be solved as a 1-body problem. Reduced mass, , is defined as: . Calculate the reduced mass for H2 and D2. Convert the molecular weights from g/mol to kg using *N*A so the units work out later.
2. The vibrational frequency of a molecule, , can be derived using simple harmonic motion considerations: , where *k* is the force constant of the “spring.” Calculate the vibrational frequency of H2 and D2 given that *k*HH = 574.9 N/m and *k*DD = 577.0 N/m (normally one would calculate the force constant from experimental data). Convert  in Hz to cm-1 (wavenumber) using c = .
3. The zero point energy of a vibration, E0, is given by: E0 = ½ h, where h is Planck’s constant, h = 6.626·10-34 J·s. This is the position of the lowest vibrational state of a bond above the minimum energy of the classical potential energy curve. In chemical reactions, we are normally concerned with the vibration of the bond that will be broken during the reaction. What is the zero point energy of H2 and of D2 in J? in kJ/mol? Draw the respective ZPEs in a potential energy well (sample shown below).

 

1. Typical C-H and C-D stretches are 3000. cm-1 and 2120. cm-1. Calculate the C-H and C-D force constants and the zero point energies of those bonds. Draw the respective ZPEs in a potential energy well.
2. The Rh-H and Rh-D stretches are reported in the paper to be 2000 cm-1 and 1414 cm-1. Calculate the Rh-H and Rh-D force constants and the zero point energies of those bonds. Draw the respective ZPEs in a potential energy well.

**Part 2: Reading guide for Jones and Feher**

1. What is microscopic reversibility?
2. What is a kinetic isotope effect (KIE), in English.
3. How specifically are equations (2) and (3) different? Why are the *k*H/*k*D ratios so different for the two reactions? *Hint:* the authors use this to make an important argument about the rate-determining step of the reaction.
4. What do you think happens to the H or D present on compound (**3**) when it reacts with CCl4 (explain the quenching reaction).
5. On page 4816, the authors say “benzene is not labile … under the conditions of the experiment.” What does this mean? Why is this important?
6. What is a linear transition state? Why would having one make the KIE larger?
7. In part 1 of this reading guide, you calculated the ZPEs for C-H and C-D bonds. The rate of a reaction depends on the height of the activation barrier, ∆G‡, and the rate constant k is proportional to e^(-∆G‡/RT). In a reaction with a regular KIE, say, breaking a C-H bond with a linear transition state, there would significant C-H/D bond breaking at the transition state. Which compound, C-H or C-D will have the larger barrier? Why?
8. Consider a reaction coordinate free energy diagram for C-H/D bond breaking and calculate the maximum possible KIE (kH/kD) for such a reaction at 298 K. To do this, it may help conceptually to assume that the barrier from the ground state to the transition state is some value, E1. The exact value of E1 will turn out to be unimportant as it appears in both the H and D reactions and will be subtracted out of the final answer. For the starting material, there is an intact C-H/D bond, while at the transition state, assume no C-H/D bond and therefore no C-H(D) ZPE.
9. An inverse kinetic isotope effect is one where kH/kD < 1. Does it make sense that you would ever get an inverse kinetic isotope effect for a C-H(D) bond-breaking reaction? Why or why not?
10. The reaction from compound **3** to compound **2** (Scheme I and Scheme III) goes through an intermediate that is unlabeled in the paper. For convenience, define that unlabeled intermediate as compound **42**. In the first step of the reaction, which *does* have an inverse KIE, there is significant C-H/D bond character present at both compound **42** and at the transition state between **3** and **42**. In the starting material, there is a fully formed Rh-H/D bond. Carry out a similar analysis to the one you carried out in question 8 for the Rh-H/D bond breaking and C-H/D bond forming reaction to show how they calculated a KIE of 0.52. Note that the authors studied the kinetics of this reaction at 51.2 °C. Also note that your answers in questions 8 and 9 involve *breaking* a C-H(D) bond, while your answer in this question involves *making* a C-H(D) bond.
11. Explain how Scheme III shows that there is an inverse KIE going from compound **3** to compound **42**, and where that inverse KIE comes from. You should use data from the paper (the relative magnitudes of ∆1-∆5), the proposed mechanism, and your results from quesiton 10 to support your statements.
12. Why would the investigation of the rate of CH3D reductive elimination be so valuable? Why couldn’t they determine its rate?
13. On the top right side of page 4816, the authors propose and discount another possible arene activation pathway. What evidence exists to discount this mechanism?
14. Classify all of the species described in equation 1 and Scheme 1 using CBC notation, provide their electron counts, their ligand bond numbers, the valence on each rhodium and the dn count for each rhodium.
15. Name the organometallic reaction type (e.g. olefin insertion) in each step of this reaction:
a. Catalyst Initiation (**1->2**)
b. Arene coordination (**2->42**)
c. **42->3**