

A Halpern Classic
Due: October 10, 2017

Pwen Boon Chock and Jack Halpern "Kinetics of the Addition of Hydrogen, Oxygen, and Methyl Iodide to Some Square-Planar Iridium(I) Complexes," *JACS*, **1966**, 88, 3511-3514; Jack Halpern "Oxidative-Addition Reactions of Transition Metal Complexes," *Accts. Chem. Res.* **1970**, 3, 386-392.

1. Consider Table I of *JACS*, **1966**, 88, 3511. What is the electronic effect of halide on the electron density about Iridium? What data allows you to make this conclusion?
2. Why is the $\nu(\text{CO})$ value of entry 4 of Table 1 higher than that of entry 1?
3. Calculate the shift of $\nu(\text{Ir-H})$ expected as the Hydride is changed into a deuteride. Compare your prediction with the observed for $\text{IrClH}_2(\text{CO})(\text{PPh}_3)_2$ and $\text{IrClD}_2(\text{CO})(\text{PPh}_3)_2$. Why does the $\nu(\text{CO})$ value not change with the isotopic label change?
4. According to the $\nu(\text{CO})$ values contrast the donating ability of Me to that of H in these compounds. What might you expect if Me were replaced by CF_3 ?
5. CO is said to be a "reporter" ligand. What does this mean to you?
6. Why does the O_2 molecule and the H_2 molecule add in a cis geometry while the MeI addition results in a trans arrangement of Me-Ir-I.
7. From the data in Table III of *JACS*, **1966**, 88, 3511, what is the effect of changing X in $\text{IrX}(\text{CO})(\text{PPh}_3)_2$ from Cl to Br to I on the H_2 oxidative addition reaction rate? Contrast that to the same data for the MeI oxidative addition rates. To what might you ascribe the difference? NB: This is also presented in terms of Activation Parameter data in Table IV or in Table II of the *Accounts of Chemical Research* paper. Is the Eact data consistent with your conclusion derived from relative rate data? Why or why not?
8. What do you expect would be the effect of phosphine ligands on the reaction rate of MeI addition? Say for example you had a series of PPh_3 , PMePh_2 , PPhMe_2 , PMe_3 , PF_3 , and $\text{P}(\text{OEt})_3$. (Note: You might have to go to Tolman's electronic factors of ligands to figure this one out.)
9. Do you expect $\text{Me}(\text{C}=\text{O})\text{Br}$ to have a greater or slower rate than the oxidative addition of MeBr to the Ir(I) complex? The same mechanism? Why or why not?