Reading Guide for "Energetics and Mechanisms of Carbon-Carbon and Carbon-Iodide Reductive Elimination from a Pt(IV) Center," Goldberg, K. I.; Yan, J.; Breitung, E. M. *J. Am. Chem. Soc.* **1995**, *117*, 6889-6896. **DOI:** 10.1021/ja00131a010

In the introduction to this paper, the authors explained why they carried out the study of the mechanism of C-C or C-I reductive elimination. Given that "most industrially significant applications of homogeneous transition metal catalysis" involves both oxidative addition and reductive elimination, better understanding the "energetics and mechanisms" of these reactions will aid future development of these catalysts. Reductive elimination (at the time) was usually more difficult to study due to the thermodynamics of the reaction: it is enthalpically disfavored relative to oxidative addition.

Consult Figures 2 and 3 from the paper. Complex **1** is [(dppe)PtMe$_3$I], and it can lose either MeI to form complex **2** [(dppe)PtMe$_2$] or ethane to form complex **3** [(dppe)PtMeI].

1. What are the major experimental differences between the reactions described in these two figures? Why did they make those changes?

2. Use the data shown in Figure 3 (in the 100-200 minute time region) to estimate the value of the equilibrium constant between (dppe)PtMe$_3$I and (dppe)PtMe$_2$ + MeI?

3. How are the enthalpy and entropy of the reaction described in Figures 2 and 3 obtained from the data in the Van ‘t Hoff plot shown in Figure 4? A Van ’t Hoff plot relates equilibrium constants with reciprocal absolute temperature: $\ln K = \frac{-\ \Delta H^\circ}{R}\left(\frac{1}{T}\right)$ (y = ln(K), x = 1/T (Kelvin), R = 8.314 J/mol·K). *Hint, you will need your K_{eq} from the previous problem.*

The relatively small value of ΔH found above is what allows for the equilibrium seen in Figures 2 and 3 and thus easier observation of the RE reaction. The enthalpy of the C-I RE (Reductive Elimination) reaction was found to be +66 kJ/mol while the enthalpy of the C-C RE was found to be -105 kJ/mol. The energies of activation ($\Delta H^\ddagger$ and $\Delta S^\ddagger$) were found using an Eyring plot (plot of ln(k) vs 1/T, shown in Figure 7 in the paper). From this data, the authors ascribed values for the Pt-C and Pt-I bonds (described on page 6892). This part of the paper should be viewed through the lens of history as being flawed. While the ΔH of the reactions and the reaction coordinate free energy diagrams are correct, ascribing these energies to a specific bond breaking or bond making steps is wrong. Unlike organic chemistry, where it is reasonable to assume a C-C bond is a C-C bond is a C-C bond, there are so many structural rearrangements, oxidation state changes, and other factors that make one Pt-C bond very different from another Pt-C bond, and bond strength tables are not as readily available. The take home message is that the attribution of a M-C or M-I bond strength based on the data presented in the paper is incorrect.

4. Explain Figure 9. a) what does it show? b) can you use this Figure to explain the long time point results shown in the inset of figure 3?

5. Are the reactions from 2 to “A” to 1 in Scheme 2 the microscopic reverses of the reactions from 1 to “A” to 2? Why or why not?

The data in this paper does in fact rule out one possible mechanism for RE. Direct attack of iodide on **1** to give an anionic intermediate is ruled out due to the lack of rate dependence on iodide that would be observed for the reaction shown in Scheme 3. The first step of the RE is instead loss of iodide to solution followed by rapid external attack of free I^- to make CH_3I.