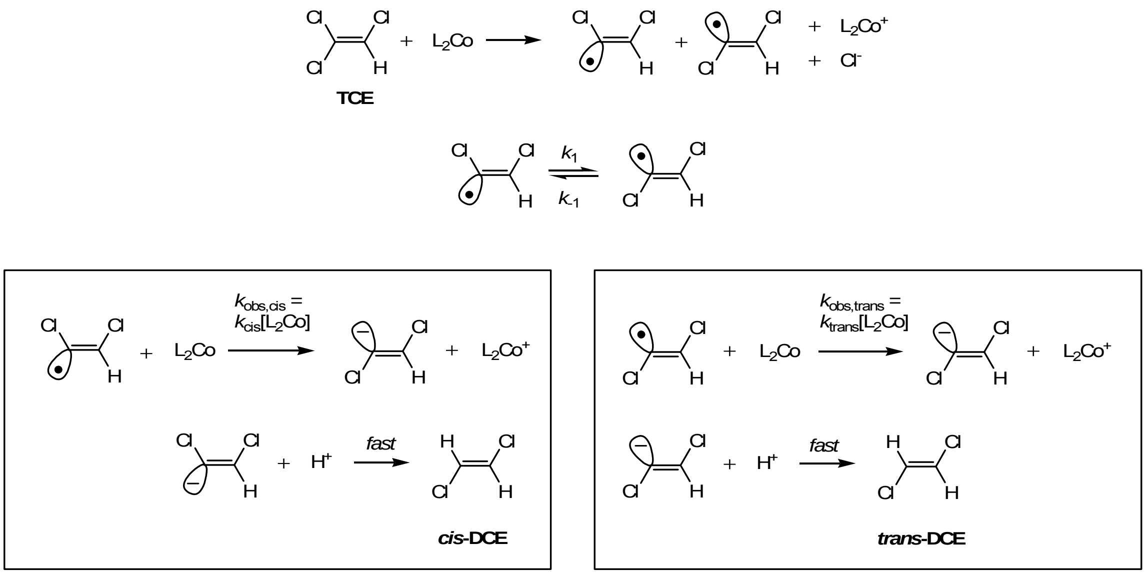
Chemistry 4011/8011 Monday, October 30

Section Question 7

Angela Follett and Kris McNeill have investigated the mechanism of how the pollutant trichloroethylene (**TCE**) is degraded to *cis*- and *trans*-dichloroethylene (**DCE**) in the environment and in model solutions.[1] Using the model reductant cobaltocene (**L_2Co**), they noted that the ratio of products produced depends on the concentration of reductant. To explain this, they suggested the following mechanism:



a. Sketch a potential energy diagram for the overall process. Helpful to know:

- *cis*-DCE$^{\bullet}$ (radical) is slightly more stable than *trans*-DCE$^{\bullet}$;
- *cis*-DCE^{-} (anion) is significantly more stable than *trans*-DCE^{-}.

b. What might you guess about the relative energies of the *cis*- and *trans*-transition states for the reduction of DCE$^{\bullet}$ to DCE^{-}, based on the information above?

c. Follett and McNeill hypothesized that the relative amounts of *cis*- and *trans*-**DCE** produced varied with [**L_2Co**] because, under their reaction conditions, k_1, k_{-1}, $k_{obs,trans}$ and $k_{obs,cis}$ were of similar magnitude. What would determine the ratio of products under the extreme case [**L_2Co**] $\rightarrow 0$? What about where [**L_2Co**] $\rightarrow \infty$? Under which of these cases would the Curtin-Hammett principle apply?

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[1] Follett, A. D.; McNeill, K. *J. Am. Chem. Soc.* **2005**, *127*, 844-845.