QUIZ #1 (100 points)

Answer all questions as completely as you can. Clearly show your work and reasoning.

1. Epoxidation is a typical reaction of alkenes. Use the bond energies given below to estimate the exothermicity of a hypothetical catalytic epoxidation of an alkene by hydrogen peroxide. (50 pts)

\[
\Delta H(\text{reaction}) = -\text{enthalpy of product bonds made} + \text{enthalpy of reactant bonds broken}
\]

\[
\Delta \text{E}(\text{C-C}) = 85 \text{ kcal/mol}, \Delta \text{E}(\text{C-O}) = 87 \text{ kcal/mol}, \Delta \text{E}(\text{C}=\text{C} \text{ pi}) = 65 \text{ kcal/mol}, \Delta \text{E}(\text{O-O}) = 51 \text{ kcal/mol}, \
\Delta \text{E}(\text{C-H}) = 98 \text{ kcal/mol}, \text{three-ring strain} = 27.6 \text{ kcal/mol}.
\]

\[
\Delta \text{H}(\text{reaction}) = \{2(\text{C-O}) - (\text{O-H})\} + (\text{C}=\text{C} + \text{O-O} + \text{O-H}) \text{ (three bonds made, three bonds broken)} + \text{strain}
\]

\[
= -2(87) - (119) + 27.6 + 65 + 51 + 119 + 27.6 \text{ (strain is + on products side, anti-enthalpic)}
\]

\[
= -30 \text{ kcal/mol}, \text{a substantially exothermic reaction, despite three ring formation}
\]

\[
\Delta \text{H}(\text{I}) = \text{C(H)3(Cd)} + \text{C(H)2(Cd)2} + \text{Cd(C)(C)} + \text{Cd(C)(H)} + \{\text{cyclopropane strain with internal alkene}\}
\]

\[
= -10.1 + (-4.3) + 10.3 + 8.6 + 53.7 \text{ (only one strain correction per ring)}
\]

\[
= +58.2 \text{ kcal/mol}
\]

\[
\Delta \text{H}(\text{II}) = 2\text{C(H)2(C)(Cd)} + \text{Cd(C)(C)} + \text{Cd(H)(H)} + \{\text{cyclopropane fused to sp2 carbon}\}
\]

\[
= 2(-4.8) + 10.3 + 6.3 + 40.9
\]

\[
= +47.9 \text{ kcal/mol}
\]

\[\text{II is thermodynamically preferred (less positive enthalpy of formation). Since it is isolated from the reaction and is most stable, it is likely that it is formed first (though not a sure thing), so this fits the pseudoenthalpic model. Note that the most substituted alkene is not the most stable in this particular case (due to ring strain!).}\]