What is Evans Polanyi Principle?

Evans-Polanyi Principle (a.k.a. Bell-Evans-Polanyi Principle, EP)

There usually exists a linear relationship between the activation energy ($E_A$ or $\Delta H^\ddagger$) and enthalpy of reaction ($\Delta H$). “The more stable reaction product is formed via the lower-energy TS”

For a series of analogous (or related) reactions:

- **Endothermic reactions**: an increase in the positive enthalpy of reaction there is an increase in the activation energy.
- **Exothermic reactions**: an increase in the negative enthalpy of reaction there is a decrease in the activation energy.

The above energy diagram shows that for the reactions represented with solid lines, the reaction with the highest energy TS has the highest energy products (and the lowest energy TS leads to the lowest energy products). Note however, the rxn that produces the
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benzyl radical does NOT follow EP principle! There are some other exceptions to the EP principle.

Hammond Postulate (5th Ed of text Ch4 pg 164)

The transition state (TS) is more similar in structure to the species (reactant/starting material or products) to which it is more similar in energy.

For an individual reaction:
Endergonic ($\Delta G > 0$) reactions: T.S. is similar in E and structure to the products
Exergonic ($\Delta G < 0$) reactions: T.S. is similar in E and structure to the reactants/starting material

For a series of analogous (or related) reactions:
Increasingly endergonic reactions: T.S. is increasingly similar to products
Increasingly exergonic reactions: T.S. is increasingly similar to the reactants/starting material

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\[
\Delta H \quad \text{[kcal/mol]}
\]

Reaction Coordinate

ΔH [kcal/mol]
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Reaction coordinate for the addition of “H+” to 2-methylpropene to form the primary isobutyl and tertiary tert-butyl cations (more stable b/c more hyperconjugation stabilized more substituted carbocation) – TS for form of tert-butyl cation is lower in E b/c also stabilized by hyperconjugation (Hammond Postulate states that the TSs look more like the carbocation products b/c they are closer in energy (b/c endergonic reaction).

Combine both EP and Hammond must be used to discuss the kinetics of a given reaction!