# The Hammond Postulate: Transition States, Energy Diagrams, and Reaction Selectivity — Study Guide

The Hammond Postulate is one of the most broadly applicable principles in all of organic chemistry. Once you truly understand it, you can predict the selectivity of reactions you have never seen before simply by knowing whether the key step is exothermic or endothermic. This guide builds from first principles through energy diagrams to applications across the course. Drawing on Hammond's original 1955 paper, Clayden, Wade, McMurry, and Chemistry LibreTexts.

# 1. What is a Transition State? Revisiting the Reaction Coordinate

Before the Hammond Postulate makes sense, you need a clear mental picture of what a transition state is and how it sits on an energy diagram.

## The Reaction Coordinate Diagram

Every elementary reaction step can be plotted on a reaction coordinate diagram: energy on the y-axis, progress of bond breaking and forming on the x-axis. The x-axis is not time — it is how far along the chemical transformation has gone, from reactants on the left to products on the right.

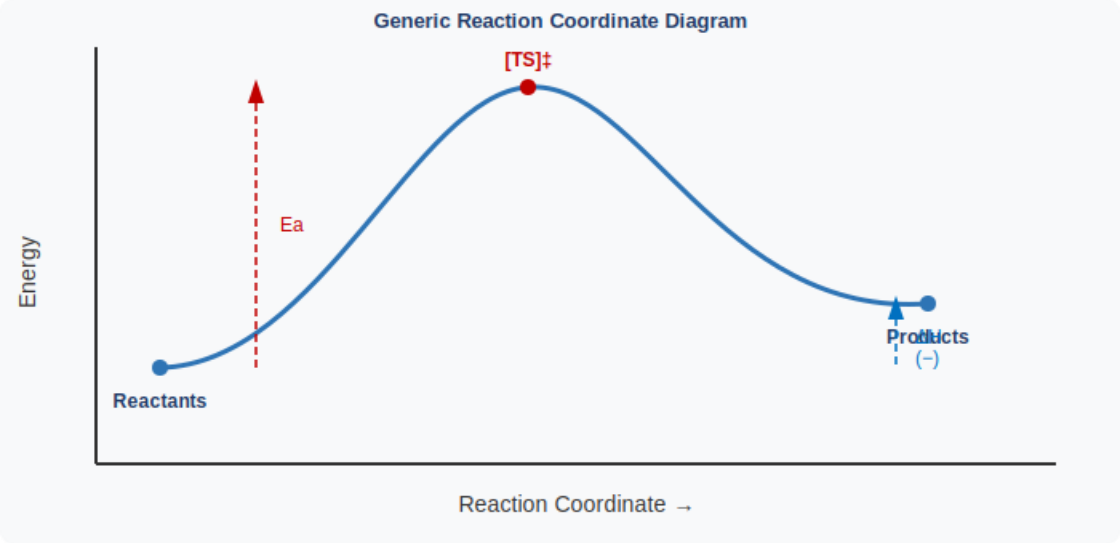


*Figure 1. Generic reaction coordinate diagram showing reactants, transition state, products, Ea, and ΔH.*

Key features:

- Reactants: starting point at a defined energy level on the left.
- Products: ending point at a defined energy level on the right.
- Transition state (TS): the peak of the energy curve — the highest-energy point on the path. It is NOT a stable species. It cannot be isolated, stored, or detected directly.
- Activation energy (Ea): energy difference between reactants and the TS. Higher Ea = slower reaction.
- ΔH: energy difference between reactants and products. Negative = exothermic; positive = endothermic.

## Transition State vs Intermediate: A Critical Distinction

| Feature | Transition State (TS) |
|---|---|
| **Energy position** | Peak of energy curve |
| **Stability** | Unstable; instantly collapses forward or back |
| **Bonds** | Partially formed / partially broken |
| **Isolable?** | No — never |
| **Notation** | Brackets with ‡ superscript: [A···B]‡ |
| **Examples** | [R···H···Br]‡ in H-abstraction |

A common exam mistake is confusing a TS with an intermediate. Intermediates sit in energy valleys and can (in principle) be trapped. Transition states are fleeting saddle points on the energy surface that exist for femtoseconds and cannot be isolated under any conditions.

# 2. The Hammond Postulate: Statement and Logic

George Hammond published his postulate in 1955. It addressed a practical problem: transition states cannot be observed directly, so how can we reason about their structure and energy?

## The Original Statement

> *If two states, as for example a transition state and an unstable intermediate, occur consecutively during a reaction process and have nearly the same energy content, their interconversion will involve only a small reorganization of the molecular assemblage. — G. S. Hammond, J. Am. Chem. Soc. 1955, 77, 334.*

## Plain-Language Version

> *The transition state of a reaction step resembles whichever species is closest to it in energy — the reactants (if exothermic) or the products (if endothermic).*

## The Logic

Think about the geometry of the energy curve. The TS sits at the peak. If the products are much lower in energy than the reactants (strongly exothermic), the peak is close to the reactant level and comes early on the x-axis. If the products are much higher (strongly endothermic), the peak is close to the product level and comes late on the x-axis.

| Step Thermodynamics | TS Position |
|---|---|
| **Strongly exothermic** | Early |
| **Slightly exothermic** | Slightly early |
| **Thermoneutral** | Middle |
| **Slightly endothermic** | Slightly late |
| **Strongly endothermic** | Late |

> The Hammond Postulate is an approximation that works best when comparing closely related reactions — such as 1° vs 2° vs 3° H-abstraction by the same radical. It is the standard tool for predicting selectivity in organic chemistry exams and research.

# 3. Energy Diagrams: Exothermic Steps and Early Transition States

We now build the energy diagram for an exothermic reaction step. We use chlorine radical H-abstraction from an alkane as our example.

*R–H + Cl• → R• + HCl  ΔH ≈ −2 to −5 kcal/mol (exothermic)*

## Diagram: Exothermic H-Abstraction (Chlorination)

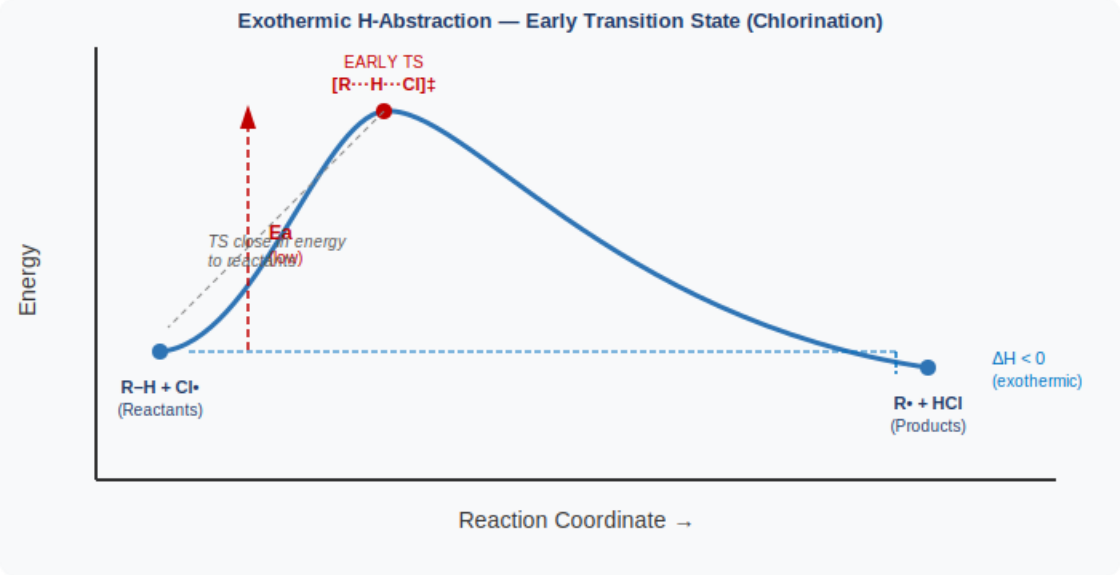


*Figure 2. Energy diagram for exothermic H-abstraction by Cl•. The TS appears early on the reaction coordinate, close in energy to the reactants.*

## Reading the Diagram

- Reactants (R–H + Cl•) and TS are close in energy — low activation energy.
- TS appears early on the x-axis: very little C–H bond breaking has occurred at the TS.
- Products (R• + HCl) are significantly lower in energy than reactants.
- Because the TS resembles the reactants, the structure at the TS is still very close to R–H + Cl•. Very little radical character has developed on carbon.

## What This Means for Selectivity

Because little radical character has developed at the TS, the stability difference between a 1°, 2°, or 3° radical barely registers in the TS energy. The energy curves for 1° and 3° abstraction are nearly identical:

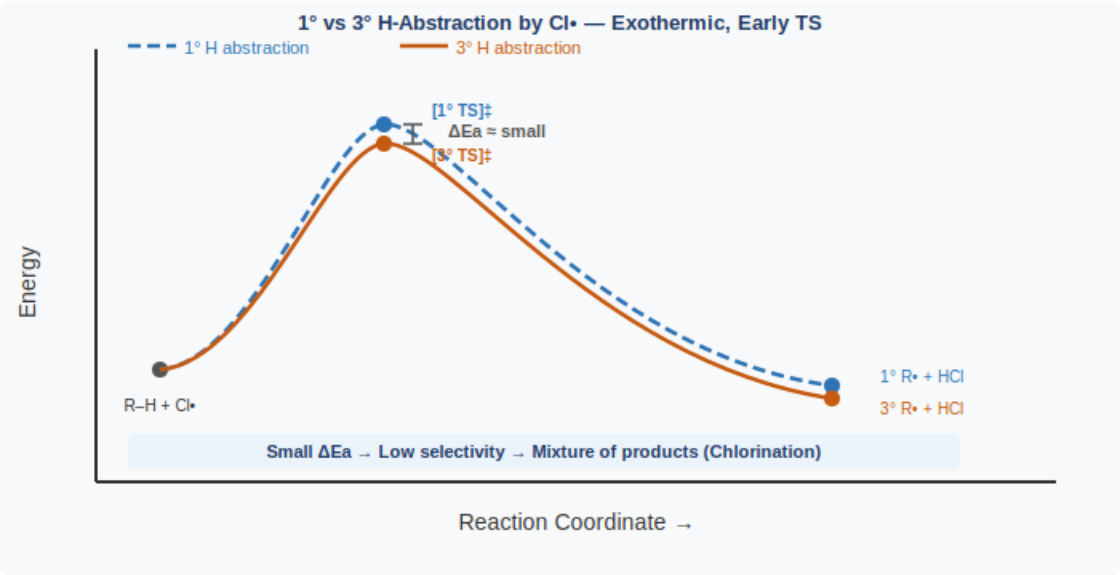


*Figure 3. Chlorination: 1° vs 3° H-abstraction by Cl•. The two transition states are very close in energy (small ΔEa), giving low selectivity.*

The 3° TS is only slightly lower than the 1° TS because the TS is early and radical character is minimal. Both positions are nearly equally accessible, so chlorination gives a statistical mixture of products with limited selectivity (~5:1 per H for 3° vs 1°).

# 4. Energy Diagrams: Endothermic Steps and Late Transition States

Now we build the energy diagram for an endothermic H-abstraction step. We use bromine radical as our example — the contrast with chlorine is stark.

*R–H + Br•  →  R• + HBr     ΔH ≈ +5 to +18 kcal/mol (endothermic)*

## Diagram: Endothermic H-Abstraction (Bromination)

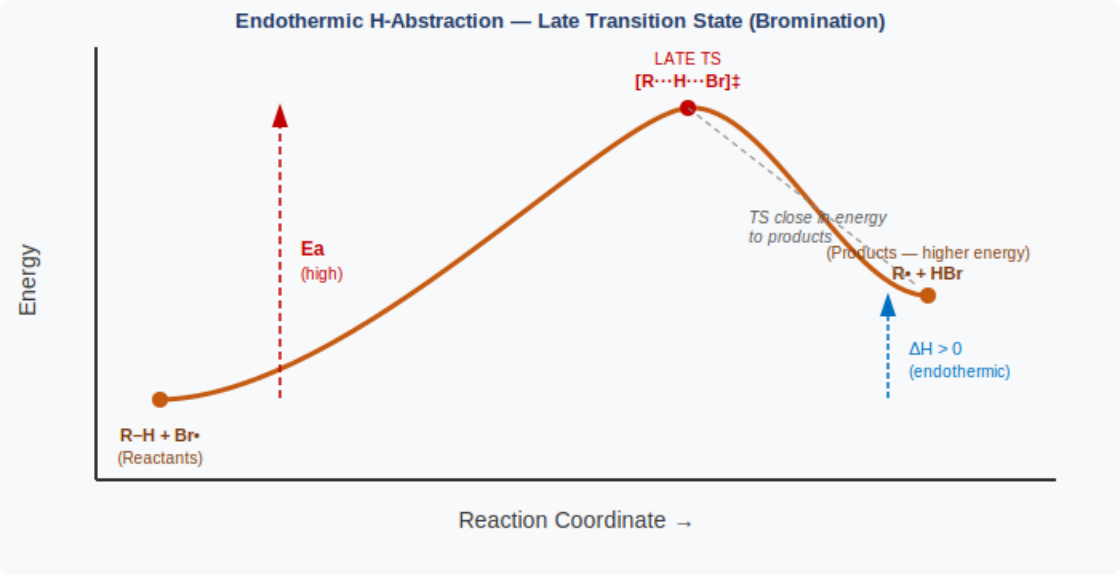


*Figure 4. Energy diagram for endothermic H-abstraction by Br•. The TS appears late on the reaction coordinate, close in energy to the products (R• + HBr).*

## Reading the Diagram

- Products (R• + HBr) are significantly HIGHER in energy than reactants — endothermic step.
- TS appears late on the x-axis: substantial C–H bond breaking has occurred. The carbon center already has significant radical character.
- TS and products are close in energy. The TS closely resembles the product radical R•.
- Therefore, the stability of R• directly controls the TS energy: a more stable radical gives a meaningfully lower TS.

## Selectivity: 1° vs 3° by Br•

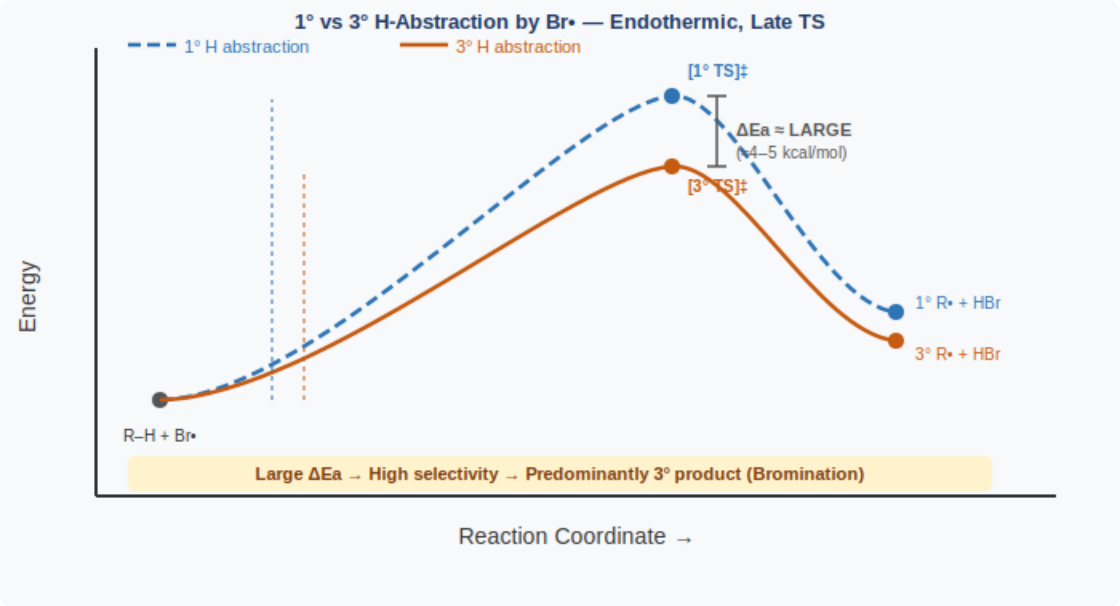


*Figure 5. Bromination: 1° vs 3° H-abstraction by Br•. The large stability difference between 1° and 3° radicals translates into a large ΔEa, giving excellent selectivity (~1600:1 per H for 3° vs 1°).*

The 3° radical is ~4–5 kcal/mol more stable than a 1° radical. Because the TS is late and closely resembles the radical, this full stability difference appears in the TS energy gap. A 4 kcal/mol difference in Ea translates to ~1000-fold selectivity at room temperature via the Arrhenius equation. Bromination is essentially completely selective for the most substituted position.

> Remember: the energy difference between radical types is the same for chlorination and bromination (~4–5 kcal/mol). What changes is how much of that difference shows up at the TS. Early TS = barely any shows up. Late TS = nearly all of it shows up. This is the entire mechanistic basis of the selectivity difference.

# 5. Application: Chlorination vs Bromination Selectivity

With the full energy diagram picture established, we can directly compare the two reactions side by side.

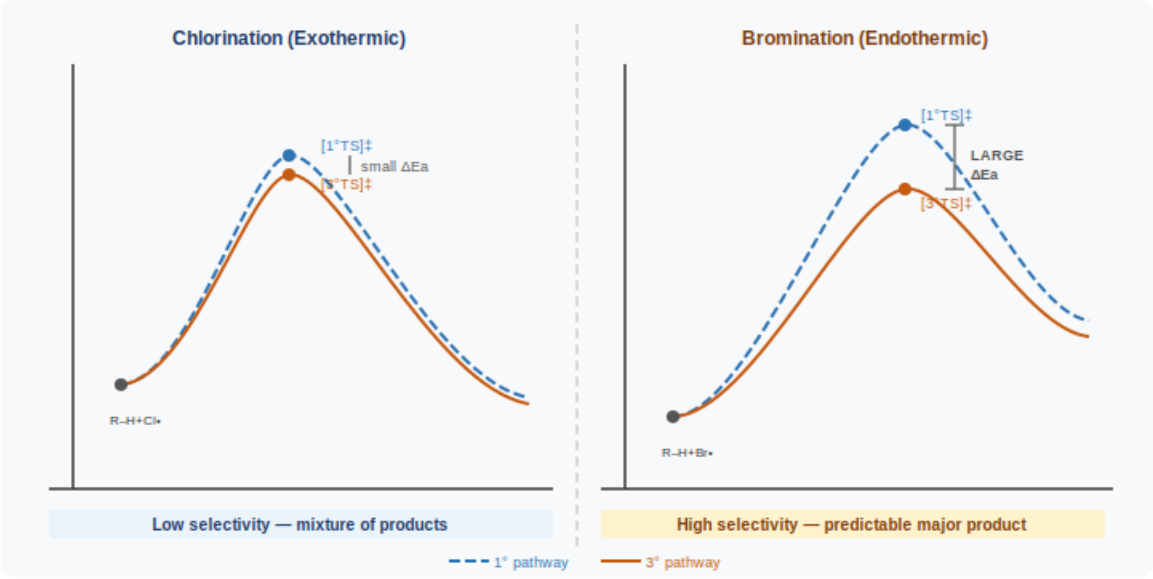


*Figure 6. Side-by-side comparison of chlorination (left) and bromination (right). Chlorination shows nearly identical TS energies for 1° and 3° pathways (low selectivity). Bromination shows a large TS energy gap (high selectivity).*

| Feature | Chlorination (Cl• + R–H) | Bromination (Br• + R–H) |
|---|---|---|
| **ΔH of H-abstraction** | ~−2 to −5 kcal/mol (exothermic) | +5 to +18 kcal/mol (endothermic) |
| **TS position** | Early (reactant-like) | Late (product-like) |
| **C–H breaking at TS** | Minimal (<25%) | Substantial (>75%) |
| **Radical character at TS** | Small | Large |
| **3° vs 1° ΔEa** | ~0.5–1 kcal/mol | ~4–5 kcal/mol |
| **3° vs 1° selectivity per H** | ~5:1 | ~1600:1 |
| **2° vs 1° selectivity per H** | ~4.5:1 | ~82:1 |
| **Practical outcome** | Mixture of products | Highly predictable single major product |

## The Reactivity–Selectivity Principle

> *A highly reactive reagent is less selective. A less reactive reagent is more selective. High reactivity means low Ea, which means an early TS, which means intermediate stability barely registers in the TS energy.*

Cl• is more reactive (exothermic H-abstraction, low Ea, fast) but less selective. Br• is less reactive (endothermic H-abstraction, high Ea, slow) but exquisitely selective. The cost of selectivity is rate. This trade-off appears throughout organic chemistry.

# 6. Application: Why More Stable Intermediates Form Faster

The Hammond Postulate is the mechanistic foundation for several rules you have already learned. In each case, the logic is identical: an endothermic step has a late TS that closely resembles the intermediate, so the intermediate's stability controls the rate.

## SN1 Reactions: Carbocation Formation

The rate-determining step of SN1 is ionization of the C–X bond to form a carbocation. This step is endothermic. By Hammond, the TS is late and resembles the carbocation. Therefore, the stability of the carbocation directly controls the activation energy.

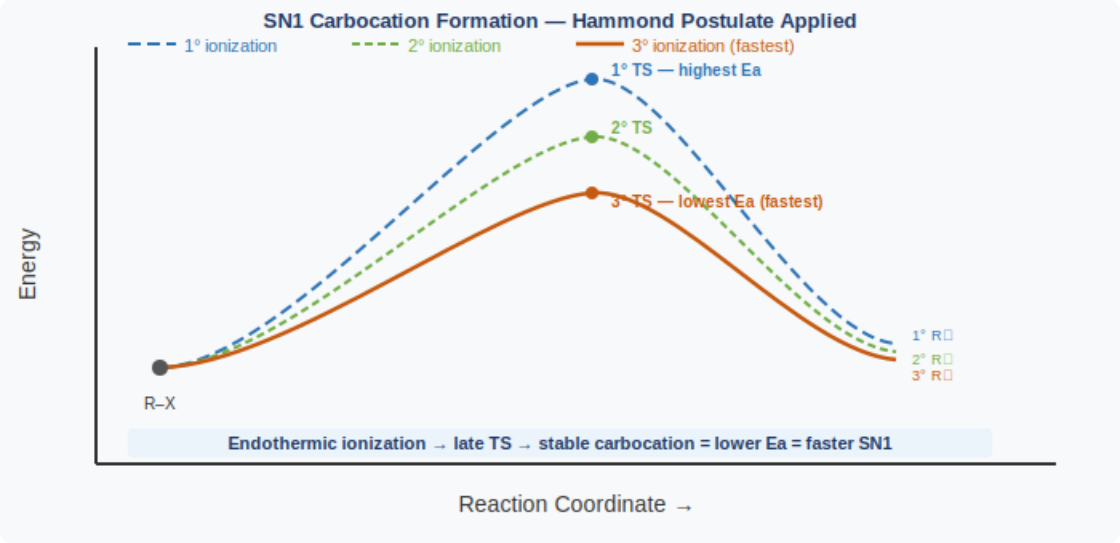


*Figure 7. SN1 carbocation formation. The endothermic ionization step has a late TS resembling the carbocation product. More stable (3°) carbocation = lower TS = faster ionization. This is why SN1 is limited to 3° (and sometimes 2°) substrates.*

- 3° carbocation is most stable → lowest TS energy → fastest ionization → SN1 works well.
- 2° carbocation is moderate → higher TS → slower, possible under some conditions.
- 1° carbocation is very unstable → very high TS → SN1 essentially never occurs at primary substrates.

## Markovnikov's Rule: HX Addition to Alkenes

When HX adds to an unsymmetrical alkene, the proton can bond to either carbon. The step that forms the carbocation is endothermic. By Hammond, the TS is late and resembles the carbocation. The more stable carbocation forms faster:

$CH_2{=}CHCH_3 + H^+ \rightarrow CH_3{}^+CHCH_3$ *(2°, more stable) → faster → Markovnikov product*

$CH_2{=}CHCH_3 + H^+ \rightarrow {}^+CH_2CH_2CH_3$ *(1°, less stable) → slower → minor product*

This is Markovnikov's rule, derived mechanistically from the Hammond Postulate. The rule is not an empirical coincidence — it is a direct consequence of endothermic carbocation formation having a late TS.

## Carbocation Rearrangements

When a less-stable carbocation forms in an endothermic step, the activation energy for 1,2-hydride or 1,2-alkyl shifts to a more stable carbocation is low — because the TS for these shifts also resembles the more stable cation being formed. Rearrangements proceed in the direction that gives a more stable carbocation because that direction has the lower TS energy.

# 7. Hammond Across the Course: A Reference Map

| Reaction / Concept | How Hammond Applies |
|---|---|
| **Radical halogenation: $Br_2$ vs $Cl_2$** | Endothermic H-abstraction (Br•) → late TS → radical stability controls selectivity |
| **SN1 substrate requirements** | Endothermic ionization → late TS → stable carbocation = lower Ea = faster rate |
| **Markovnikov's rule (HX + alkene)** | Endothermic protonation → late TS → more stable carbocation forms faster |
| **E1 and Zaitsev's rule** | Endothermic carbocation formation → same logic as SN1 |
| **Carbocation rearrangements** | Late TS for rearrangement steps → more stable cation = lower TS = faster shift |
| **Allylic/benzylic radical selectivity** | Endothermic H-abstraction by Br• → resonance-stabilized radical lowers TS dramatically |
| **Acid-base: endothermic proton transfer** | Late TS → stability of conjugate base controls activation energy and rate |

## The Core Insight

> *Whenever a step is endothermic, the TS resembles the products, and the stability of the product intermediate directly controls the rate and selectivity of that step. Whenever a step is strongly exothermic, the TS resembles the reactants and intermediate stability barely matters.*

## Quick Recap

| Concept | Key Point |
|---|---|
| **Transition state** | Energy peak; partial bonds; cannot be isolated; drawn as [A···B]‡ |
| **Intermediate** | Energy valley; full bonds; can persist briefly; can sometimes be trapped |
| **Exothermic step** | Products lower; TS early; resembles reactants; intermediate stability ≈ invisible |
| **Endothermic step** | Products higher; TS late; resembles products; intermediate stability controls rate |

| | |
|---|---|
| **Hammond Postulate** | TS resembles the species closest to it in energy on the reaction coordinate |
| **Reactivity–selectivity** | More reactive reagent → lower Ea → earlier TS → less selective |
| **Bromination selectivity** | Endothermic H-abstraction → late TS → radical stability matters → high selectivity |
| **SN1/Markovnikov** | Endothermic cation formation → stable cation = lower TS = faster = major product |

- ✓ TS is always at the energy peak; it is not an intermediate and cannot be isolated
- ✓ Exothermic step → early TS → resembles reactants → intermediate stability barely matters
- ✓ Endothermic step → late TS → resembles products → intermediate stability controls rate and selectivity
- ✓ Bromination: endothermic H-abstraction → late TS → ~1600:1 selectivity for 3° over 1° per H
- ✓ Chlorination: exothermic H-abstraction → early TS → only ~5:1 selectivity for 3° over 1° per H
- ✓ Hammond explains Markovnikov's rule, SN1 substrate requirements, and carbocation rearrangements
- ✗ Don't confuse TS (energy peak) with intermediate (energy valley)
- ✗ Don't expect high selectivity from strongly exothermic steps — the early TS erases stability differences

## References & Further Reading


- Hammond, G. S. A Correlation of Reaction Rates. J. Am. Chem. Soc. 1955, 77 (2), 334–338. DOI: 10.1021/ja01607a027 (Original paper)
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