



Chemical Properties of Excited States

Molecular Photochemistry

CHEM 4801

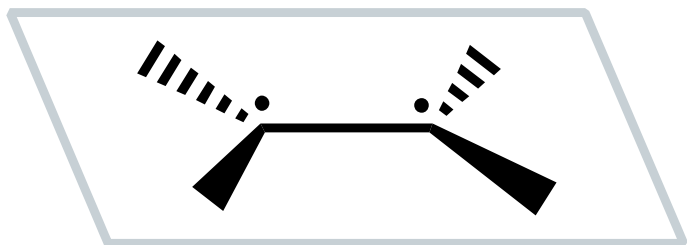
Connecting Structure and Reactivity for Excited-state Molecules

Chemical Properties of Excited States

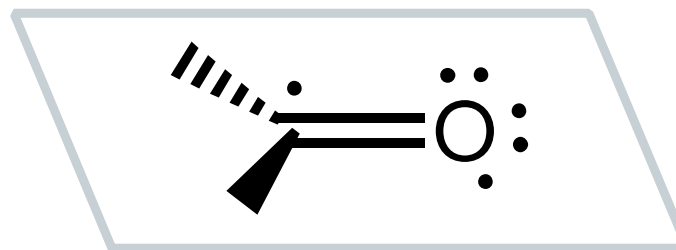
NBO Theory Revisited

The NBO configuration of an excited state provides us with a zero-order guess of its electronic structure. Drawing NBO shapes reveals the spatial distributions of electrons in excited states.

Alkene (π, π^*)



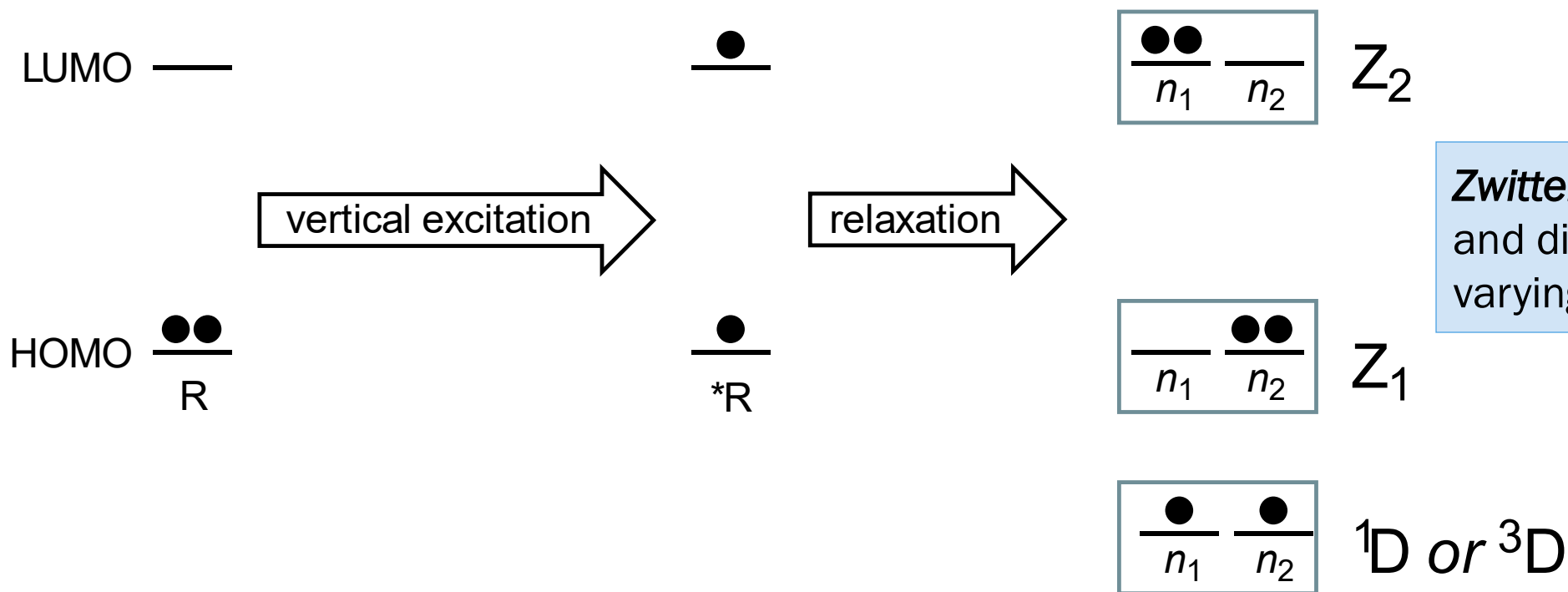
Carbonyl (n, π^*)



Considering overlap of the SOMOs also gives us insight into singlet and triplet energies and ΔE_{ST} .

Organic Excited States are Diradicaloids

A **diradicaloid** contains two electrons in orbitals of equal or similar energy. Most minima on excited-state potential energy surfaces can be viewed as diradicaloids.



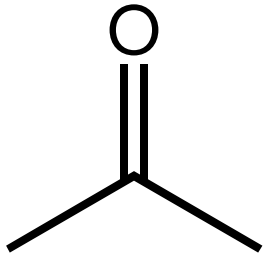
Zwitterionic states are singlets and differ in energy due to varying charge stabilization.

Triplet or singlet **diradical** states

Note that triplet $*R$ *must* evolve to form a diradical; singlet $*R$ can form either a diradical or a zwitterion.

Example: The Carbonyl Group

$n \rightarrow \pi^*$ excitation of the carbonyl group produces a structure with radical electrons on carbon and oxygen.



$h\nu$



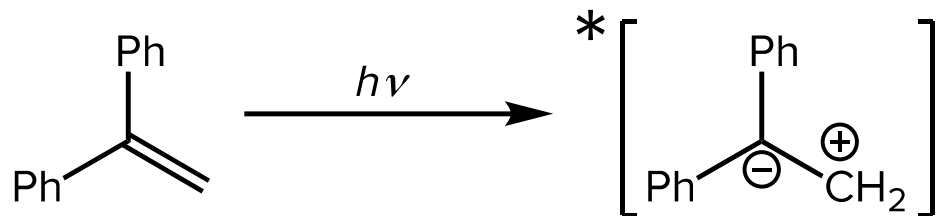
ISC



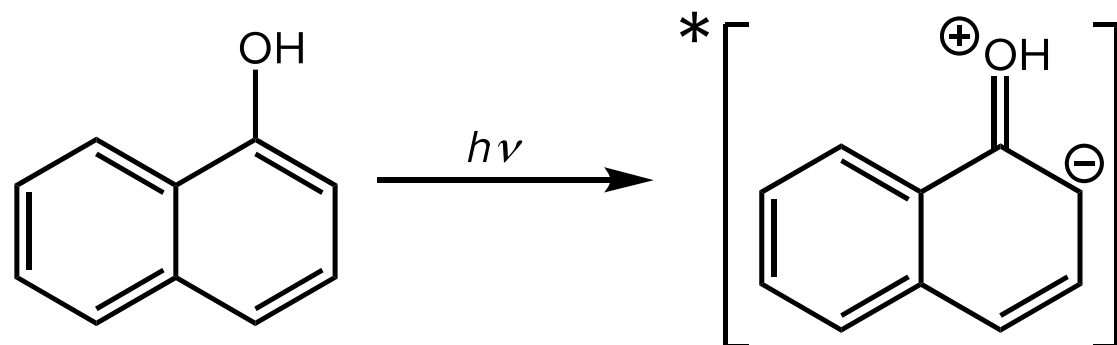
Resonance and Photoexcitation

Electronic excitation of a conjugated pi system often enhances the importance of the “second best” resonance form, which becomes a zwitterionic intermediate.

Electron transfer is enabled.



Heteroatom-substituted arenes become *much* more acidic on excitation.



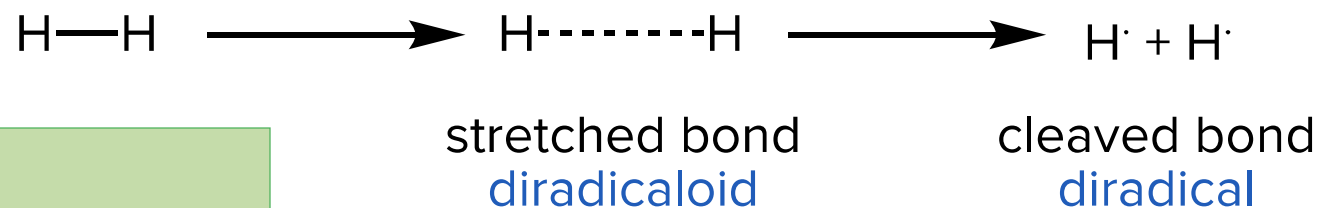
Structure	p <i>K_a</i>
R	9.2
*R	0.4

Detailed Analysis of Sigma- and Pi-bond Cleavage

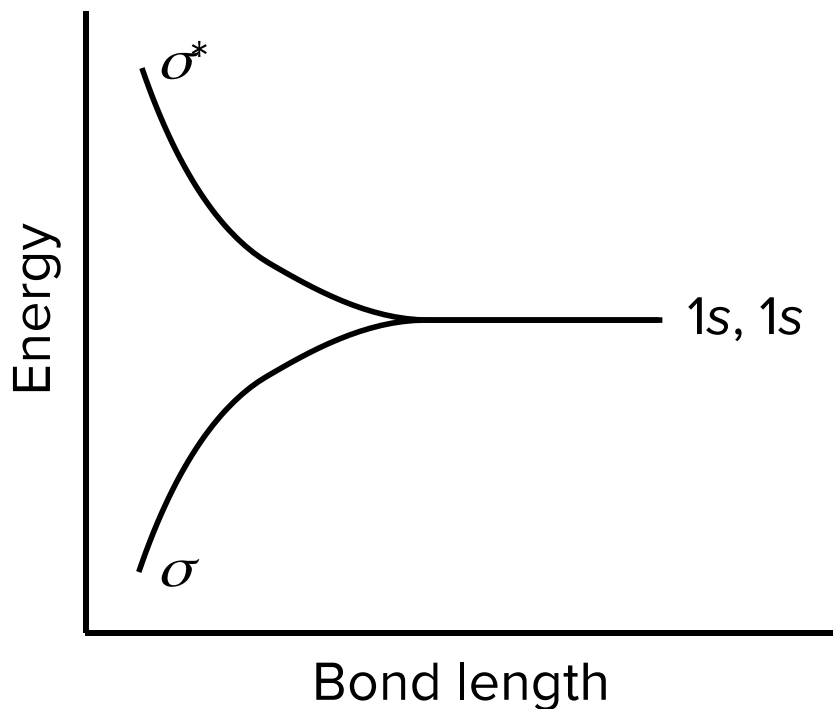
Chemical Properties of Excited States

Cleavage of a Sigma Bond

Elongation of a sigma bond produces a diradicaloid structure and a diradical. Analysis of the orbitals, configurations, and states involved provides an exemplar for *any* sigma-bond cleavage process.



Orbitals



Cleavage of a Sigma Bond

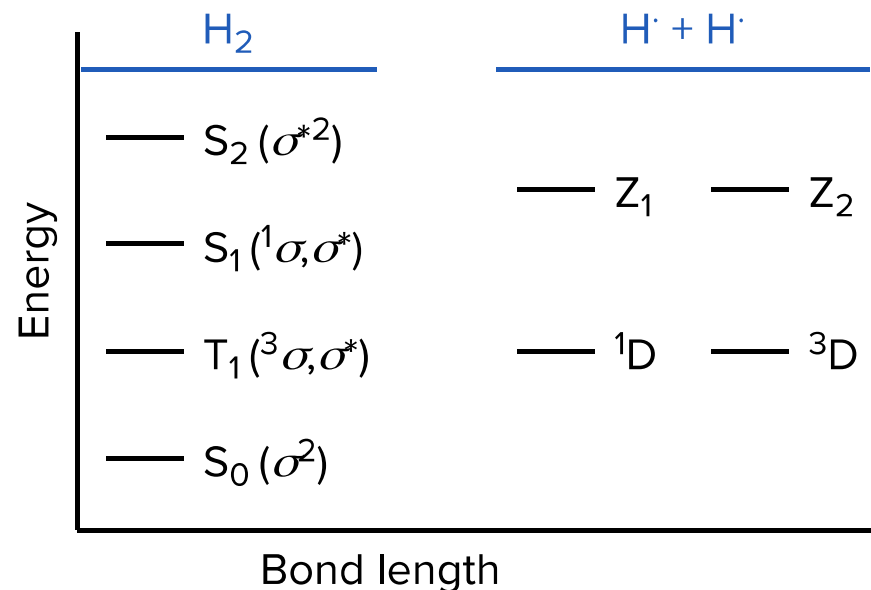
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stretched bond
diradicaloid

cleaved bond
diradical

Electron Configurations



Cleavage of a Sigma Bond

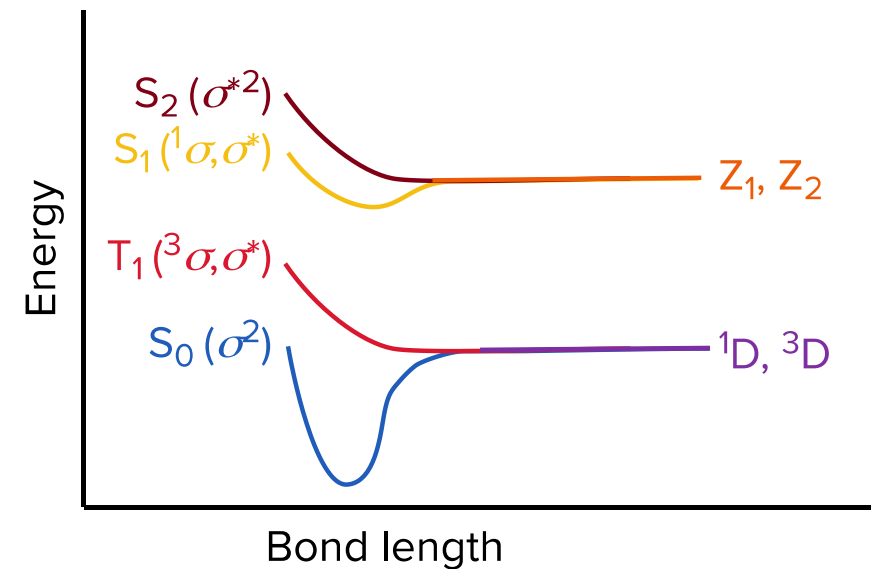
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stretched bond
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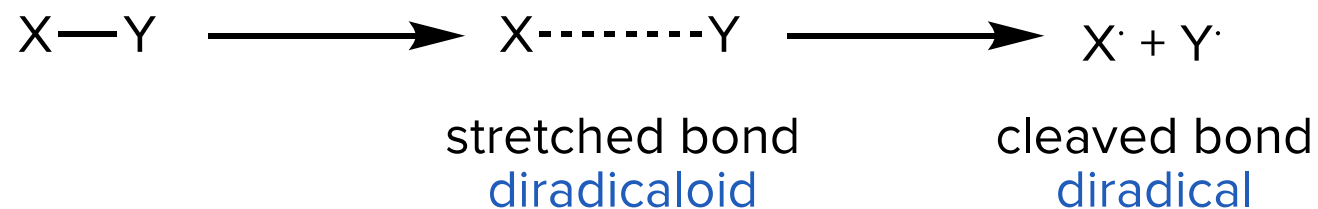
cleaved bond
diradical

Electronic States (PES)

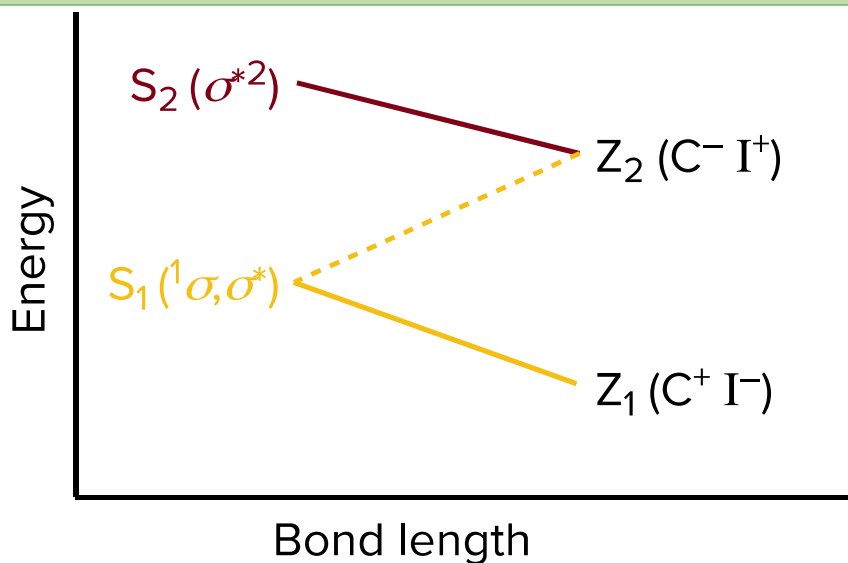


Polar Sigma Bonds

For polar sigma bonds, the energies of Z states will differ. The state with negative charge on the more electronegative atom is generally favored but S_2 correlates with the higher-energy Z_2 state.

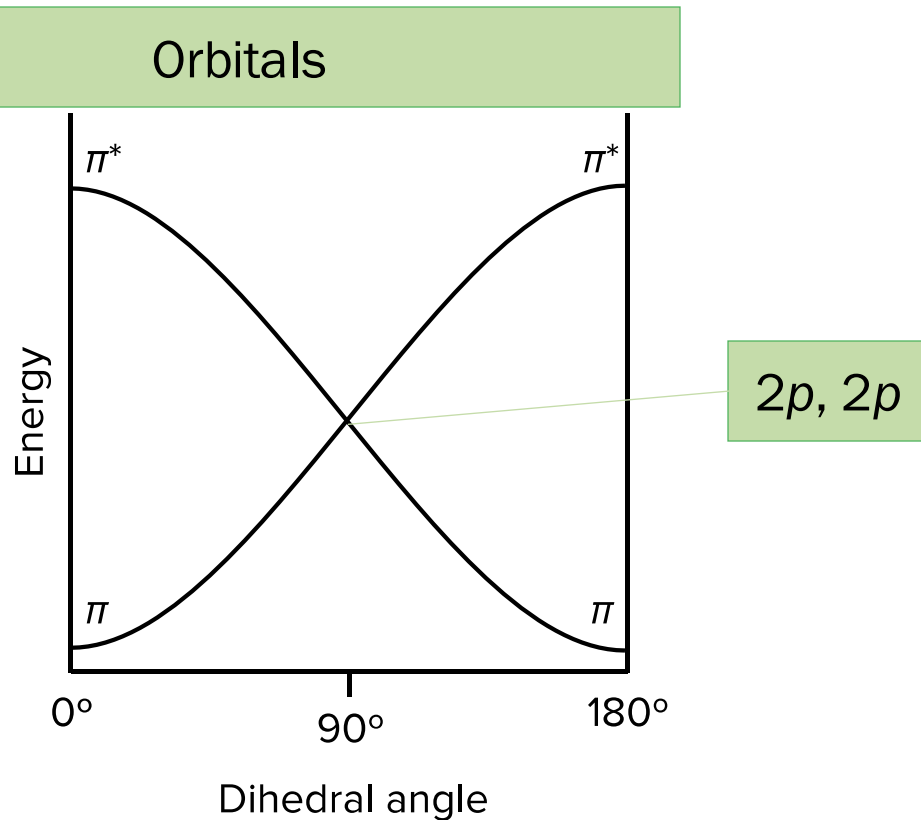
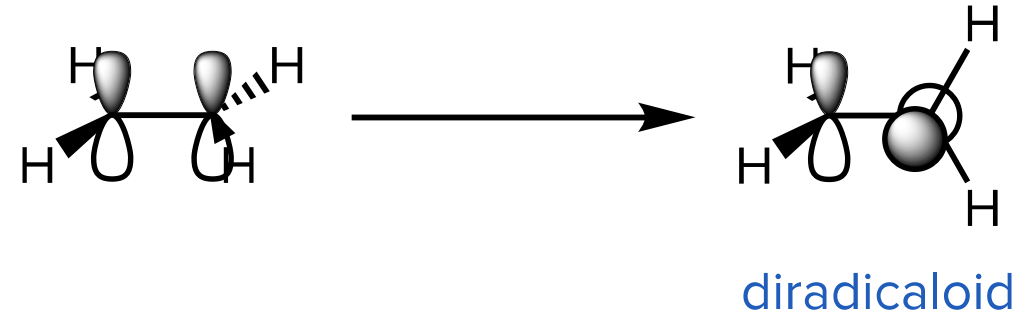


For example, when $X = C$ and $Y = I$



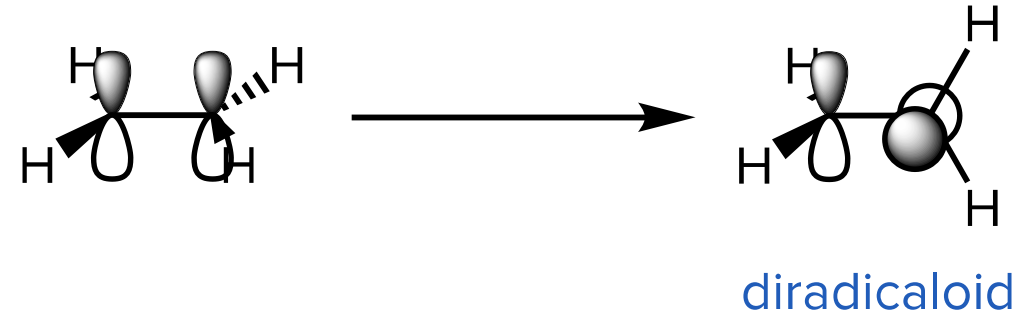
Cleavage of a Pi Bond

Rotation about the bonding axis cleaves the pi bond and produces a diradicaloid ($\theta \approx 90^\circ$) structure. Twisting of the pi bond of C_2H_4 provides an exemplar for *any* pi-bond cleavage process.

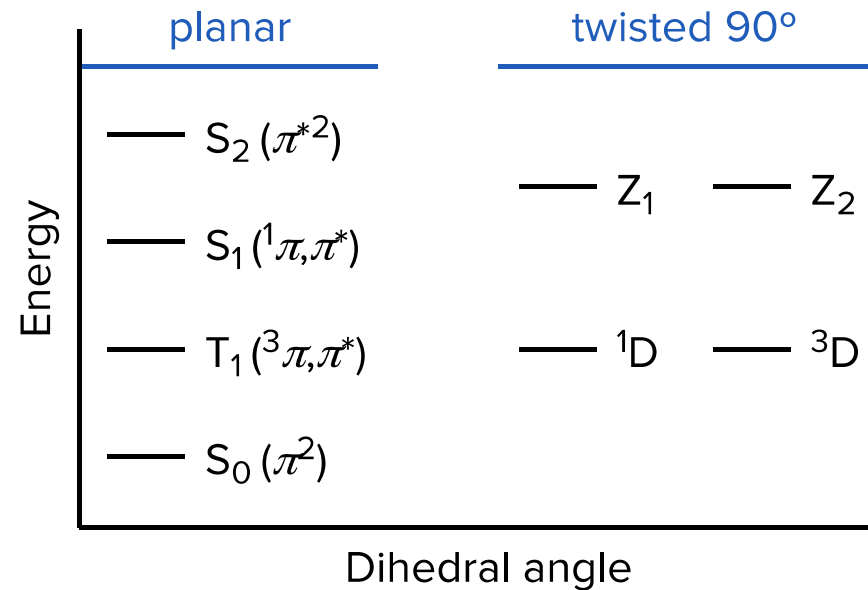


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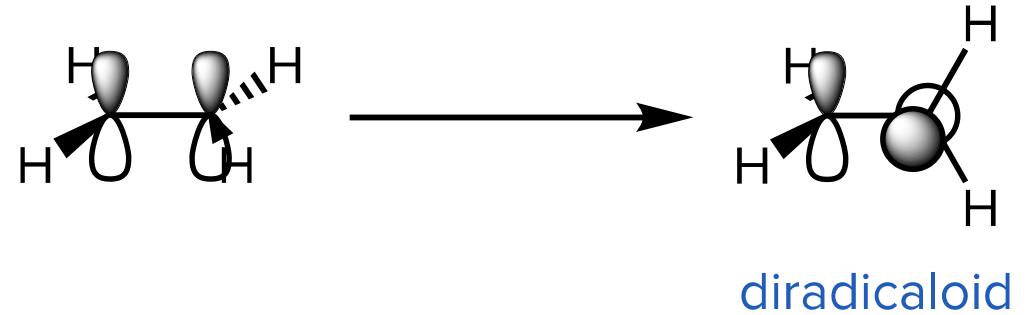
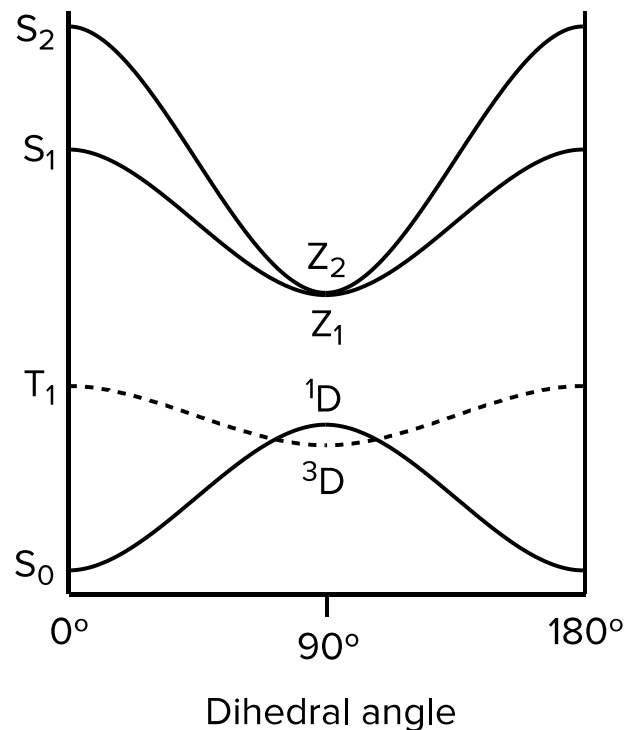
Electron Configurations



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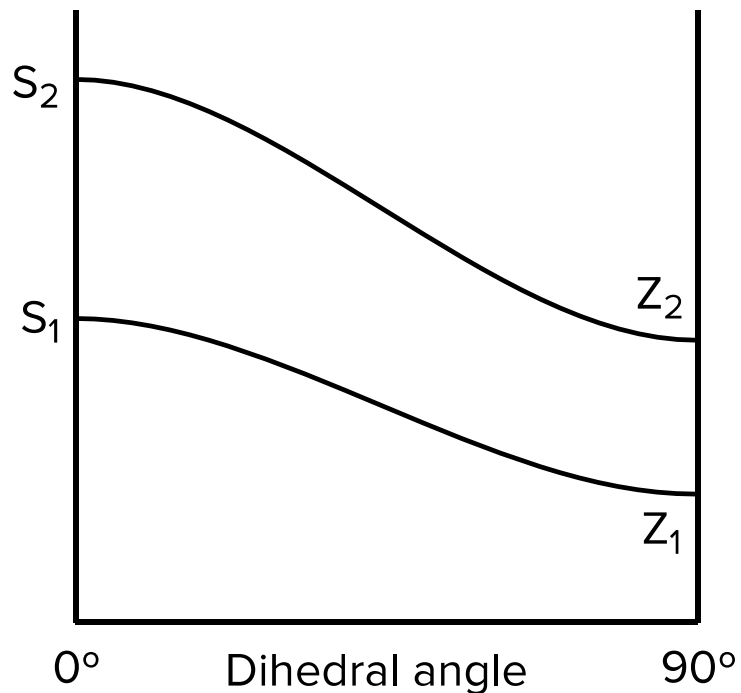
Electronic States



Polar Pi Bonds

For polar pi bonds, the energies of Z states will differ. The state with negative charge on the more electronegative atom is generally favored but S_2 correlates with the higher-energy Z_2 state.

For example, for $\text{H}_2\text{C}=\text{NH}$



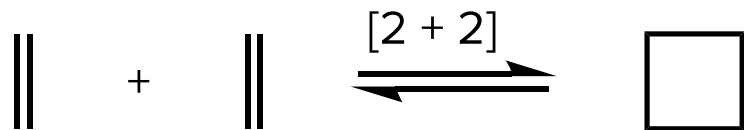
Photochemical Pericyclic Reactions

Chemical Properties of Excited States

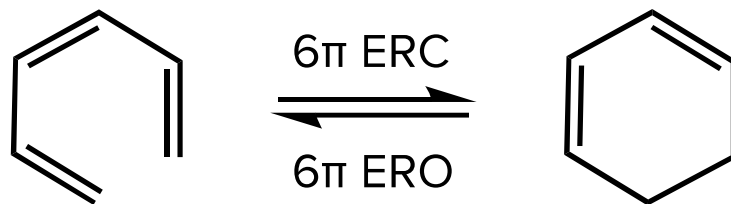
Pericyclic Reactions

Pericyclic reactions involve a concerted step in which bond reorganization occurs via a fully conjugated transition state.

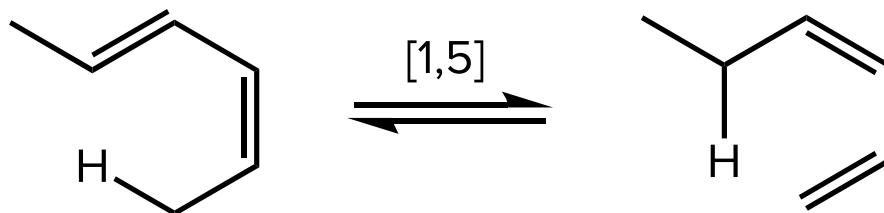
Cycloadditions
(and eliminations)



Electrocyclic
reactions



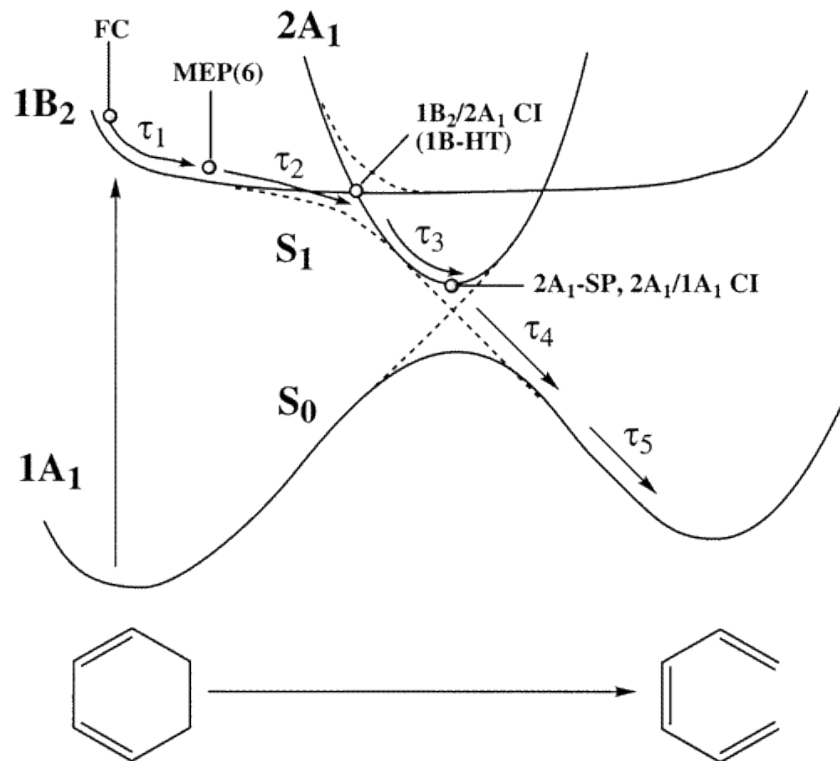
Sigmatropic
rearrangements



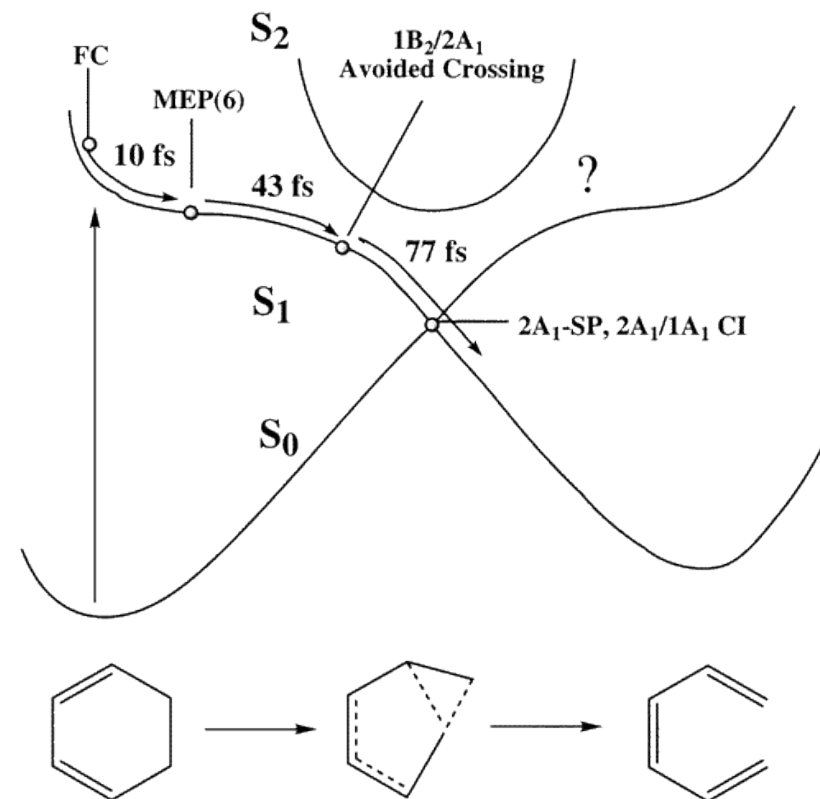
Pericyclic Reactions

Photochemical pericyclic reactions typically occur via **conical intersections** or **funnels** that connect excited- and ground-state potential energy surfaces. No intermediates are involved.

Classical conservation of symmetry



Refined model with symmetry breaking

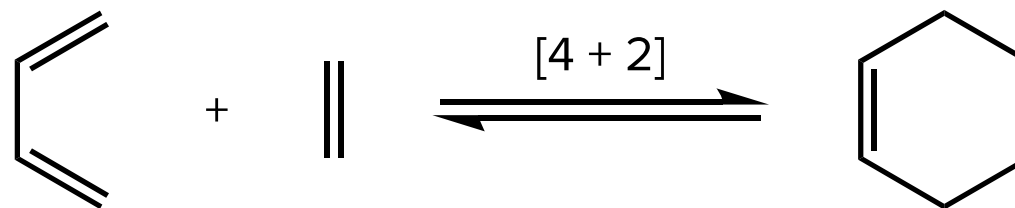
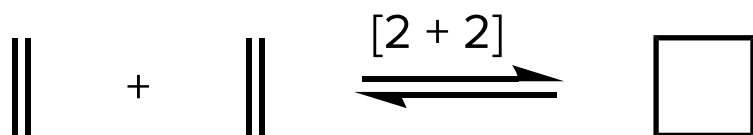


Frontier MO Analysis of Cycloadditions



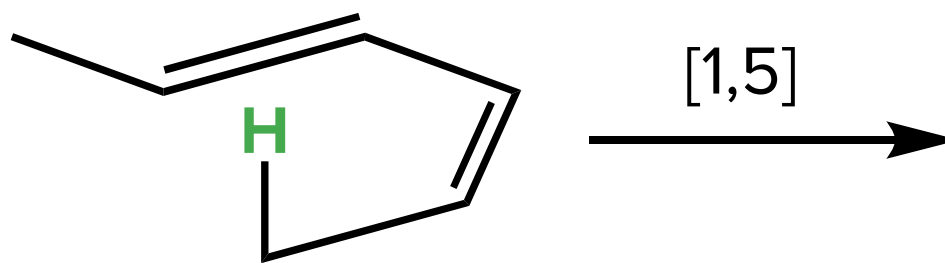
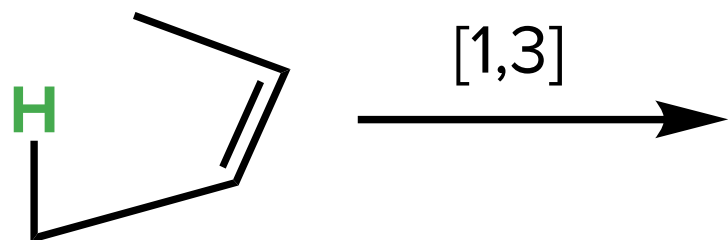
Analysis of the HOMO and LUMO of the reacting partners in a cycloaddition enables determination of whether a particular cycloaddition is *allowed* or *forbidden*.

H_LV_S^o



FMO Analysis of Sigmatropic Reactions

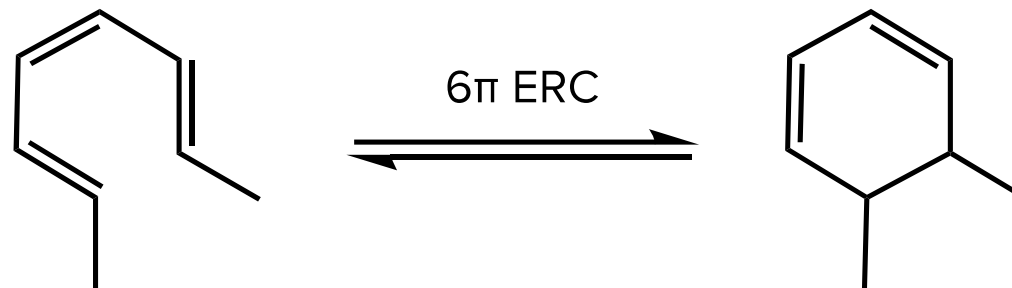
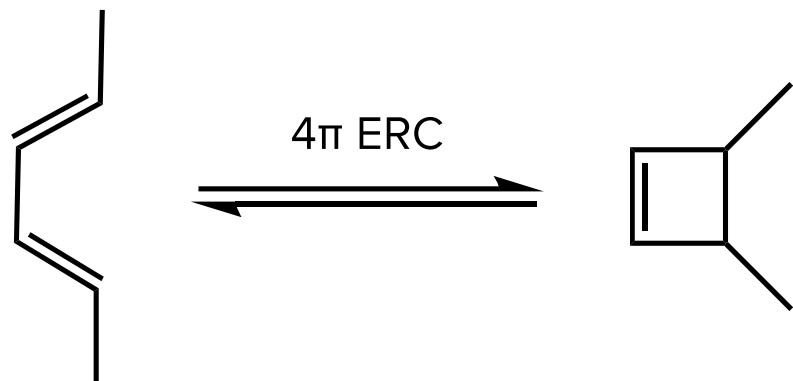
In a sigmatropic rearrangement, the HOMO and LUMO correspond to the migrating sigma bond and the pi system (or *vice versa*). The goal is to determine whether reaction will occur ***suprafacially*** or ***antarafacially***.



Orbital Symmetry in Electrocyclic Reactions



For electrocyclic reactions, we observe how the HOMO of the reactant transforms into the HOMO of the product to determine whether the reaction will be *conrotatory* or *disrotatory*.



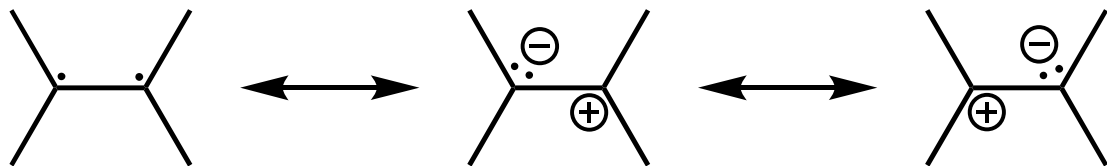
Standard Primary Photoreactions of (n,π^*) and (π,π^*) States

Chemical Properties of Excited States

Primary Reactions of (π, π^*) States

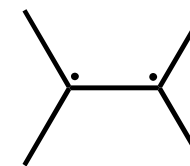
Singlet (π, π^*) states undergo pericyclic reactions and often have zwitterionic character. The latter can result in unconventional addition processes. Triplet (π, π^*) states have diradical character.

$^1(\pi, \pi^*)$



- Pericyclic reactions
 - Cycloadditions and eliminations
 - Electrocyclic reactions
 - Sigmatropic rearrangements
- Ionic reactions
 - Additions
 - Rearrangements
 - Electron transfers
- Double-bond twisting

$^3(\pi, \pi^*)$



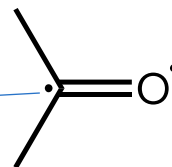
- Radical reactions
 - Atom abstractions
 - Additions to unsaturated functional groups
 - Radicaloid rearrangements
 - Homolytic bond cleavages
- Electron transfers
- Double-bond twisting

Primary Reactions of (n,π^*) States

In contrast, (n,π^*) states are essentially diradicaloid in nature regardless of spin. The reactivity of (n,π^*) under a given set of conditions depends on whether the n or π^* orbital is involved.

$^1(n,\pi^*)$ or $^3(n,\pi^*)$

π^* initiated (reactions with electrophiles)



n initiated (reactions with nucleophiles)

- Radical reactions
 - Atom abstractions
 - Radical additions
 - β -Cleavage
- Electron donation

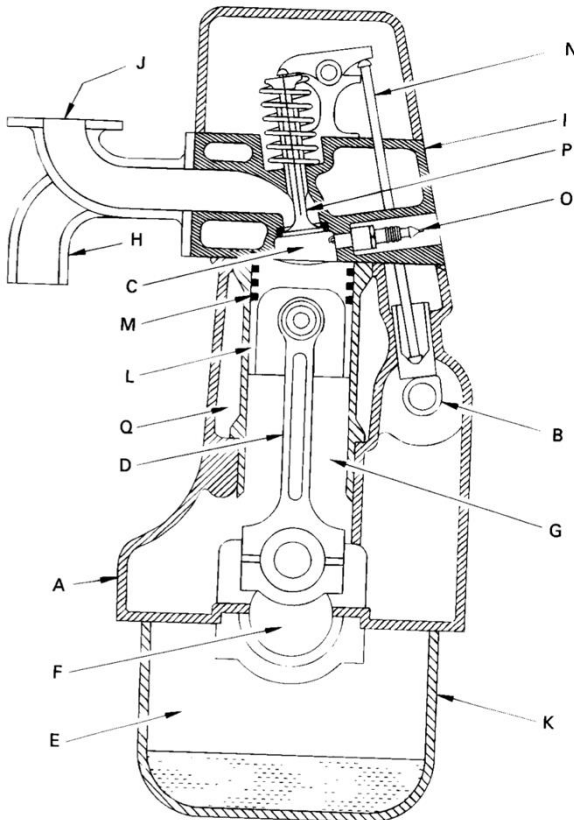
- Radical reactions
 - Atom abstractions
 - Radical additions
 - α -Cleavage
- Electron acceptance

What is a Reaction Mechanism?

Chemical Properties of Excited States

An Analogy: Mechanisms and Machines

“Mechanism” evokes the idea of a *machine*, which consists of interconnected parts operating to transmit forces, motion, and energy. Our understanding of how the parts are connected and how they operate together represents a theory on the *mechanism* of the machine.



What are the parts?

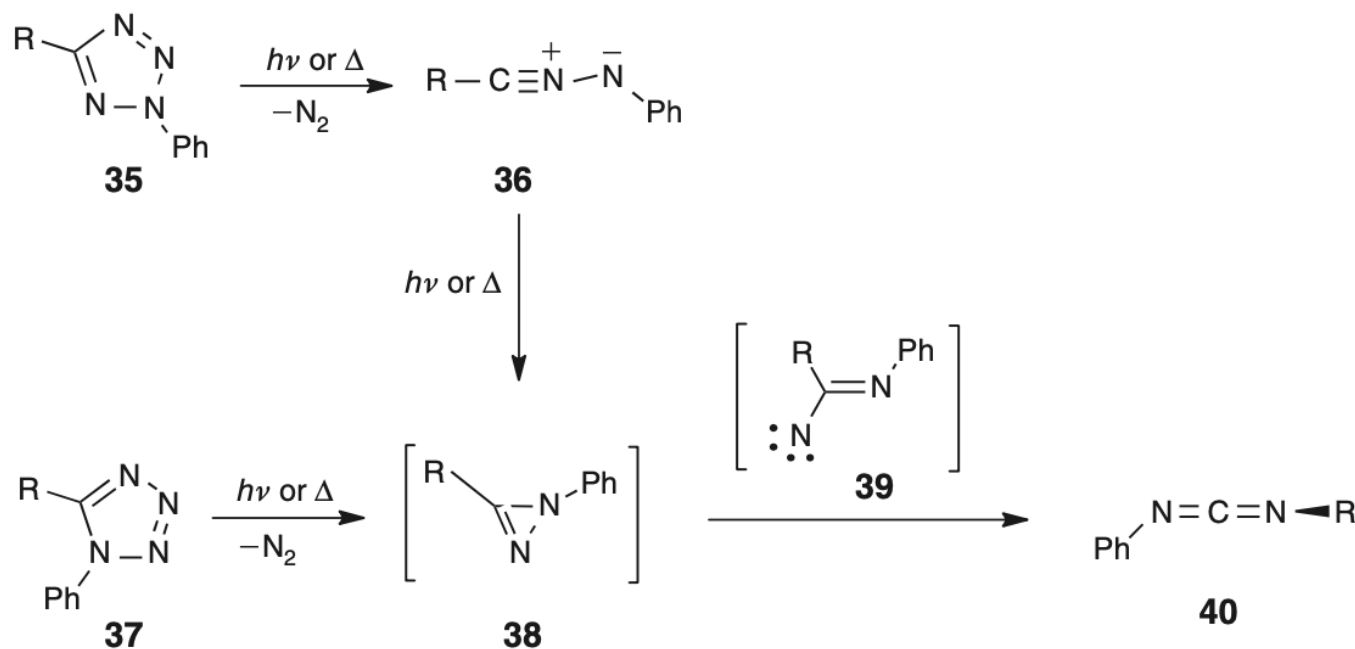
How do the parts interact?

Is our understanding of the mechanism adequate to predict and explain operation of the machine?

Figure 1-15 Cross-section of four-stroke cycle SI engine showing engine components; (A) block, (B) camshaft, (C) combustion chamber, (D) connecting rod, (E) crankcase, (F) crankshaft, (G) cylinder, (H) exhaust manifold, (I) head, (J) intake manifold, (K) oil pan, (L) piston, (M) piston rings, (N) push rod, (O) spark plug, (P) valve, (Q) water jacket.

Reaction Mechanisms

A **reaction mechanism** includes a sequence of elementary steps and molecular structures. Mechanisms allow us to predict and explain how reactions will operate under various conditions.



What are the structures of *R, I, and P?

Constitution and configuration

Spin multiplicity

What are the rate constants and efficiencies of each step?

Precedent gives us guiding principles for writing provisional mechanisms

Is the provisional mechanism consistent with the evidence?

Writing and Revising Mechanisms

Reaction mechanisms are always in a provisional state subject to revision with additional evidence.

Standard Protocol

Standard set of mechanisms
(from prior work)

Process of elimination
using data or theory

Provisional mechanisms:
A. None
B. One
C. More than one

If (A)

Devise new mechanism

Repeat standard
protocol

If (B)

Plausible mechanism
established

If (C)

Collect new data or theory
to eliminate possibilities

Repeat standard
protocol