

Pericyclic Reactions: A Glossary

Pericyclic: Involving a cyclic array of orbitals undergoing bonding changes

Concerted: Taking place in a single step, simultaneous, but not necessarily synchronous

Synchronous: Taking place at the same pace; bond making/breaking to same extent all around.

Stepwise: Involving more than one elementary steps (i.e. activation barriers) and hence having intermediates (PE minima) en route from reactant(s) to product(s).

Electrocyclic: Describes a pericyclic reaction which interconverts a polyene chain and a ring. (e.g. cyclobutene $\rightarrow$ 1,3-butadiene or hexatriene $\rightarrow$ cyclohexadiene)

Cycloaddition: A condensation of two fragments to form a ring

Sigmatropic: Migrating a σ -bonded group across a polyene system

Group Transfer: A pericyclic reaction in which a group or groups are transferred.

Suprafacial: In describing a π system as a component in a pericyclic reaction (mainly cycloaddition or sigmatropic rearrangement), this term indicates that the bonds being formed/broken at the two ends interact on the same p face. So the archetype butadiene + ethylene Diels-Alder is said to be $\pi 4s + \pi 2s$ (s = supra) where the numbers refer to the components' electron counts.

Antarafacial: Opposite of s uprafacial; interacting on opposite faces of the π component.

Aromaticity Formulation

Procedure:

Consider cyclic array of orbitals in the reaction's TS (hypothetical high symmetry). Look at the orbital phases; do they stay same (+1) at a given overlap point, or do their signs switch (-1).

Compute the product of all interactions around the ring. For example, in the case of conrotatory cyclobutene ring opening, the product = $1 \times 1 \times 1 \times (-1) = -1$ i.e. odd interaction or Mobius array.

It may help to color in atomic orbitals, but don't confuse your picture with properly analyzed symmetry adapted MOs:

Huckel array: zero or even # of sign inversions (Product = +1):

$4n+2$: Thermal Aromatic e- count

$4n$: Photochemical Aromatic e- count

Remember, all π -conjugated rings (e.g. cyclobutadiene, benzene) have Huckel topology – but aren't necessarily aromatic; that depends on e- count.

Mobius array: odd # of sign inversions (Product = -1)

$4n$: Thermal Aromatic e- count

$4n+2$: Photochemical Aromatic e- count

The Frost Circle:

Simple MO theory leads to the convenient result for Hückel and Möbius cyclic structures that their energy levels can be obtained from drawing!

Inscribe Polygon in a circle. It should have as many vertices as basis AO's. For Huckel topology, inscribe with point down; for Möbius, an edge must be down.

This makes sense: Huckel system will always have a unique all-bonding lowest E orbital, while Möbius always has at least one antibonding point.

Consider cyclobutadiene: Huckel antiaromatic system, $4n$ e-, no sign inversion.

Square cyclobutadiene's electronic structure is like the point of crossing of two orbitals of different symmetry in e.g. ethylene's 2+2 reaction to form cyclobutane. With each NBMO singly populated there is only one actual filled bonding orbital, and the compound is a diradical. It can undergo Jahn-Teller distortion to lower the E of one NBMO at the expense of the the other, but that comes at the cost of stretching bonds and pairing electrons (increasing repulsion energy). This overall analysis explains why the Huckel 2+2 reaction is thermally forbidden but photochemically allowed.

Now consider benzene: Hückel aromatic. Analogous reactions are thermally allowed, 6e- rxns. An example: disrotatory hexatriene $\rightarrow$ cyclohexadiene closure. This goes through Huckel aromatic TSs, like benzene's GS.

Cycloadditions (Aromaticity Formulation)

2 + 2

No sign inversion – Huckel 4e- cycle – antiaromatic – thermally forbidden

Two ethylenes can combine in another way that yields a Mobius aromatic cycle.

One sign inversion - 4e- cycle-thermally allowed (but sterically difficult) cycloaddition.

4 + 2

No sign inversions – Huckel 6e- cycle – aromatic – thermally allowed

In principle there is another allowed mode of combination for butadiene + ethylene; here both partners interact as antarafacial components. Again, there is an even number of sign inversions so the TS is formally aromatic. However, like the Möbius ethylene 2+2 reaction, this is a sterically somewhat difficult reaction to accomplish.