Question #61075 – Chemistry – Organic Chemistry

Question:

What is the theoretical basis of pericyclic reactions? Why is [2+2] cycloaddition reaction thermally forbidden while photo chemically allowed? Explain.

Answer:

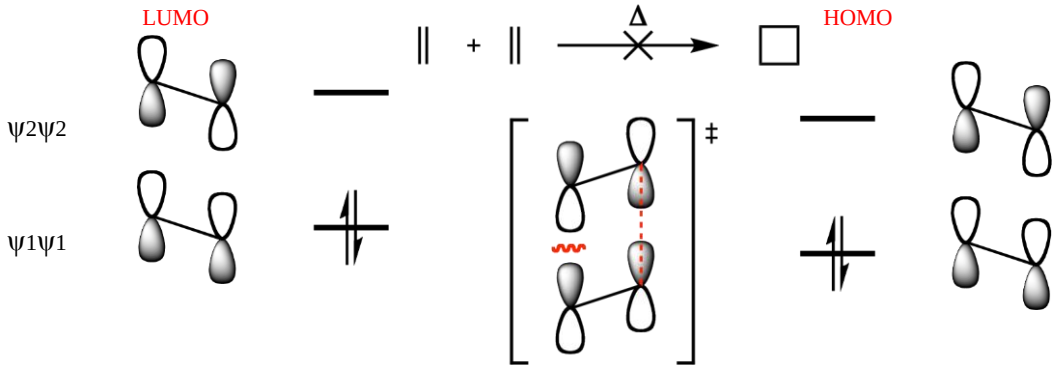
Theoretical basis of pericyclic reactions is Woodward-Hoffmann Rules

In the original publication in 1965,[4] the three rules distilled from experimental evidence and molecular orbital analysis appeared as follows:

- In an open-chain system containing 4n π electrons, the orbital symmetry of the highest occupied molecule orbital is such that a bonding interaction between the termini must involve overlap between orbital envelopes on opposite faces of the system and this can only be achieved in a conrotatory process.
- In open systems containing (4n + 2) π electrons, terminal bonding interaction within ground-state molecules requires overlap of orbital envelopes on the same face of the system, attainable only by disrotatory displacements.
- In a photochemical reaction an electron in the HOMO of the reactant is promoted to an excited state leading to a reversal of terminal symmetry relationships and reversal of stereospecificity.

The [2 + 2] Cycloaddition

Thermally, the [2 + 2] cycloaddition is geometrically forbidden, as the HOMO and LUMO of the participating olefins would not be able to achieve the orbital overlap required for σ-bond formation.



On the other hand, the photochemical [2 + 2] cycloaddition is allowed and leads to stereospecific cyclobutane formation.