Lecture 9-10 January 25-27, 2012

Rules for Chem. React. - Woodward-Hoffmann

Nature of the Chemical Bond
with applications to catalysis, materials science, nanotechnology, surface science, bioinorganic chemistry, and energy

Course number: Ch120a
Hours: 2-3pm Monday, Wednesday, Friday

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Woodward-Hoffmann rules
orbital symmetry rules
Frontier Orbital rules

Certain cycloadditions occur but not others

\[ 2s + 2s \]
\[ 2s + 4s \]
\[ 4s + 4s \]

possible transition states

Why?
Woodward-Hoffmann rules
orbital symmetry rules
Frontier Orbital rules

Certain cyclizations occur but not others

**Why?**
2+2 cycloaddition – Orbital correlation diagram
ground state

Start with 2 ethene in GS
Occupied orbitals have SS and SA symmetries
Now examine product
cyclobutane
Occupied orbitals have SS and AS symmetry
Thus must have high energy transition state: forbidden reactions
2+2 cycloaddition – Orbital correlation diagram excited state

Start with 1 ethene in GS and one in ES

Open shell orbitals have SA and AS symmetries

Now examine product cyclobutane

Open shell orbitals have AS and SA symmetry

Thus orbitals of reactant correlate with those of product

Thus photochemical reaction allowed
Consider butadiene + ethene cycloaddition; Diehls-Aldor 2+4 Ground State

Ground state has S, S, and A occupied
Product has S, A, and S occupied
Thus transition state need not be high
Allowed reaction
WH rules – 2 + 4

Excited State

Forbidden reaction

Excited state has
S, S, doubly occupied
A and S singly occupied

Product has
S, A doubly occupied
SA singly occupied

Thus transition state will be high
Forbidden reaction
Generalization WH rules cycloaddition

\[ 2n + 2m \quad \text{n+m odd: Thermal allowed} \]
\[ \quad \text{Photochemical forbidden} \]
\[ n=1, m=2: \text{ethene + butadiene (Diels-Alder)} \]

\[ n+m \text{ even: Thermal forbidden} \]
\[ \text{Photochemical allowed} \]
\[ n=1, m=1: \text{ethene + ethene} \]
Rotation, $C_2$

Conrotatory Allowed

Disrotatory Forbidden

Reflection, $\sigma$

WH rules – cyclization-GS

Butadiene
Generalization: WH rules cyclization

2n

- n even: Thermal conrotatory
- Photochemical disrotatory

- n=2 $\rightarrow$ butadiene

- n odd: thermal disrotatory
- Photochemical conrotatory

- n=3 $\rightarrow$ hexatriene
2D Reaction Surface for $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$

Product: $\text{H}_2 + \text{CH}_3$

Reactant: $\text{H} + \text{CH}_4$

Energy along reaction path

H--C

H--H

Reaction coordinate

BLYP
SVWN
GVB view reactions

Reactant HD+T

Product H+DT

Goddard and Ladner, JACS 93 6750 (1971)
During reaction, bonding orbital on D stays on D, bonding orbital on H keeps its overlap with the orbital on D but delocalizes over H and T in the TS and localizes on T in the product. Thus highly overlapping bond for whole reaction. Nonbonding Orbital on free T of reactant becomes partially antibonding in TS and localizes on free H of product, but it changes sign.
GVB view reactions

Reactant HD+T

Transition state

Product H+DT

Bond pair keeps high overlap while flipping from reactant to product

nonbond orbital keeps orthogonal, hence changes sign
Changes in VB orbitals along inversion reaction path for D+ CH\textsubscript{4} to DCH\textsubscript{3} + H
Physics behind Woodward-Hoffman Rules

For a reaction to be allowed, the number of bonds must be conserved. Consider $\text{H}_2 + \text{D}_2$

\[
\begin{array}{c}
\text{H} - \text{H} \\
\text{D} - \text{D}
\end{array} \quad \rightarrow \quad
\begin{array}{c}
\text{H} \cdots \text{H} \\
\text{D} \cdots \text{D}
\end{array} \quad \rightarrow \quad
\begin{array}{c}
\text{H} \quad \text{H} \\
\text{D} \quad \text{D}
\end{array}
\]

2 bonds \quad \text{TS} \quad \text{? bonds} \quad 2 \text{ bonds}

To be allowed must have 2 bonds at TS

How assess number of bonds at the TS. What do the dots mean? Consider first the fragment

Have 3 electrons, 3 MO’s

Have 1 bond. Next consider 4th atom, can we get 2 bonds?

Bonding 2 elect  \quad \text{nonbonding} 1 \text{ elect}  \quad \text{antibonding} 0 \text{ elect}
Physics behind Woodward-Hoffman Rules

Bonding: 2 elect
Nonbonding: 1 elect
Antibonding: 0 elect

Have 1 bond. Question, when add 4th atom, can we get 2 bonds?
Can it bond to the nonbonding orbital of the TS?

Answer: NO.
The two orbitals are orthogonal in the TS, thus the reaction is forbidden.
Summary: $\text{H}_2 + \text{D}_2 \rightarrow \text{HD} + \text{DH}$ is forbidden. The barrier is comparable to the bond energy.

The bonding phases of the reactants do NOT correlate with those of the products. Thus, the reaction is Forbidden.

Bond 1 and Bond 2 do not correlate with each other. Orbital phases do not correlate.
What about $H_2 + D_2 + T_2 \rightarrow HD + DT + TH$?

Is this allowed? Yes as flip green from $D_2$ to $DT$ and blue from $T_2$ to $TH$ get 2 phase changes in red $H$ as it moves to $D$.

Next year show sequence of orbital changes.
Selection rules for reactions
Valence bond view

Selection Rules for Chemical Reactions Using the Orbital Phase Continuity Principle
W. A. Goddard III
J. Am. Chem. Soc. 94, 793 (1972)
GVB analysis of cyclization (4 e case)

4 VB orbitals: A, B, C, D reactant

Move AB bond; Ignore D; C changes phase as moves from 3 to 1

Now ask how the CH$_2$ groups 1 and 4 must rotate so that C and D retain positive overlap.

Clearly this case (4n) is conrotatory.
Orbital analysis 4 electron cyclization (electrocyclic)

Reactant

Conrotatory TS

Phases are continuous

Product
GVB analysis of cyclization (6 e case)

Hexatriene

Cyclohexadiene

Question which rotation of the AB, CD groups maintain the phase between 1a and 1b?
GVB analysis of cyclization (6 e case)

Hexatriene

Cyclohexadiene

Question: which rotation of the AB, CD groups maintain the phase between 1a and 1b?
Answer: Disrotatory
Generalization: orbital phase continuity principle rule for cyclization

2n=4: butadiene - conrotatory

2n=6: hexatriene - disrotatory

n even: conrotatory
n odd: disrotatory
Apply GVB model to 2 + 2 cycloaddition

4 VB orbitals: A, B, C, D reactant

\[ \Phi_A, \Phi_B, \Phi_C, \Phi_D \]

4 VB orbitals: product

\[ \Phi_A, \Phi_B, \Phi_C, \Phi_D \]

TS: ignore C but maintain overlap of A with B as A delocalizes to new center

D moves but has Nodal plane
Transition state for $2 + 2$

Orbitals A on 1 and B on 2 keep high overlap as the bond moves from 12 to 23 with B staying on 2 and A moving from 1 to 3.

Orbital D must move from 3 to 1 but must remain orthogonal to the AB bond. Thus it gets a nodal plane.

The overlap of D and C goes from positive in reactant to negative in product, hence going through 0, thus break CD bond.

Reaction Forbidden
GVB model fast analysis 2 + 2

4 VB orbitals: A, B, C, D reactant

Move A from 1 to 3 keeping overlap with B

Simultaneously D moves from 3 to 1 but must change sign since must remain orthogonal to A and B

C and D start with positive overlap and end with negative overlap. Thus break bond ➔ forbidden
1. Move AB bond; Ignore D; C changes phase as it moves from 3 to 1
GVB 2+4

2. Move EF bond; C changes phase again as it moves from 1 to 5.

3. Now examine overlap of D with C. It is positive. Thus can retain bond CD as AB and EF migrate.

Reaction Allowed
1. Move AB bond; Ignore D; C changes phase as it moves from 3 to 1

2. Move EF bond; C changes phase again as it moves from 1 to 5

3. Examine final overlap of D with C. It is positive. Thus can retain bond CD as AB and EF migrate

Reaction Allowed
Summary 2+4 cycloaddition
Generalization orbital phase continuity principle rule for cycloaddition

\[ n=1, m=1: \text{ethene} + \text{ethene}: \text{forbidden} \]

\[ n=1, m=2: \text{ethene} + \text{butadience (Diels-Alder)}: \text{allowed} \]

\[ n+m \text{ even}: \text{forbidden} \]

\[ n+m \text{ odd}: \text{allowed} \]
What is best geometry for a forbidden reaction? Consider 2+2 cycloaddition

Woodward Hoffmann suggested that need to orient two ethylenes perpendicular to get them to react.

Consider that bond 1ab is moving from C12 to C23. Then the orbital 2b initially on C3 bonding to orbital 2a on C4. Must change phase as it delocalizes onto C1. Question: how must the AB on C4 move to maintain phase?
What is best geometry for a forbidden reaction? Consider 2+2 cycloaddition

Woodward Hoffmann suggested that need to orient two ethylenes perpendicular to get them to react

Consider that bond 1ab is moving from C12 to C23. Then the orbital 2b initially on C3 bonding to orbital 2a on C4. Must change phase as it delocalizes onto C1. Question: how must the AB on C4 move to maintain phase? Answer we must rotate the C34 bond out of the plane (~30°) so that the minus lobe of orbital 2a can overlap the minus lobe of 2b on C1.
Sigmatropic Reactions: [1,5] H migration

Question: Can H remain above the plane (suprafacial) as it moves from bonding to C5 to C1?
Sigmatropic Reactions: [1,5] H migration

H remains above the plane (suprafacial) as it moves from bonding to C5 to C1.
Sigmatropic Reactions: [1,3] H migration

H must go below the plane (antarafacial) as it moves from bonding to C3 to C1
Sigmatropic Reactions: [1,7] H migration

Can H remain above the plane (suprafacial) as it moves from bonding to C7 to C1
Sigmatropic Reactions: [1,7] H migration

H must move below the plane (antarafacial) as it moves from bonding to C7 to C1
Generalization orbital phase continuity principle rule for \([j,k]\) H migrations (sigmatropic)

\[j + k = 1 + 5 = 6: \text{suprafacial}\]

\[j + k = 1 + 3 = 4 \text{ and } j + k = 1 + 7 = 8: \text{antarafacial}\]

\[j + k = 4n + 2: \text{suprafacial}\]

\[j + k = 4n: \text{antarafacial}\]
Low symmetry reactions
Cylco-octatetraene $\rightarrow$ cubane?

Flip 1ab from C12 to C23 must break 3ab bond as it moves to C14
Flip 2ab from C34 to C47 must break 4ab bond as it moves from C78 to C83
Thus doubly forbidden
Butadiene + butadiene reactions

All forbidden
Can we have $2s + 2s$ reactions for transition metals?

$2s + 2s$ forbidden for organics

$\text{Cl}_2\text{Ti} - \text{Me} \quad ? \quad \text{Cl}_2\text{Ti} \quad ? \quad \text{Cl}_2\text{Ti} - \text{Me}$
Now consider a TM case: \( \text{Cl}_2\text{TiH}^+ + \text{D}_2 \)

Orbitals of reactants

GVB orbitals of TiH bond for \( \text{Cl}_2\text{TiH}^+ \)

GVB orbitals of \( \text{D}_2 \)
Is \( \text{Cl}_2\text{TiH}^+ + \text{D}_2 \rightarrow \text{Cl}_2\text{TiD}^+ + \text{HD} \) allowed?

Bonding 2 elect  
nonbonding 1 elect  
antibonding 0 elect

when add Ti 4\textsuperscript{th} atom, can we get 2 bonds?

Now the bonding orbital on Ti is d-like. Thus at TS have

Answer: YES. The two orbitals can have high overlap at the TS orthogonal in the TS, thus the reaction is allowed
GVB orbitals at the TS for
\( \text{Cl}_2\text{TiH}^+ + \text{D}_2 \rightarrow \text{Cl}_2\text{TiD}^+ + \text{HD} \)
GVB orbitals for the Cl₂TiD⁺ + HD product

Note get phase change for both orbitals
Follow the D2 bond as it evolves into the HD bond.
Follow the TiH bond as it evolves into the TiD bond
Barriers small, thus allowed

Increased d character in bond $\Rightarrow$ smaller barrier
Are all MH reactions with D2 allowed? No

Example: ClMn-H + D2

Here the Mn-Cl bond is very polar

Mn(4s-4p_z) lobe orbital with Cl:3pz

This leaves the Mn: (3d)^5(4s+4pz), S=3 state to bond to the H

But spin pairing to a d orbital would lose

4*K_{dd}/2 + K_{sd}/2 = (40+2.5) = 42.5 kcal/mol

whereas bonding to the (4s+4pz) orbital loses

5*K_{sd}/2 = 12.5 kcal/mol

As a result the H bonds to (4s+4pz), leaving a high spin d5.

Now the exchange reaction is forbidden
Show reaction for ClMnH + D2

Show example reactions
Summary

Generalized Valence Bond (GVB) calculations find that during chemical reactions the localized bonding orbitals of the reactants delocalize over 3 centers in the TS and relocalize on the atoms of the product bond, retaining the same phase (overlap) throughout the reaction.

This continuity of the phase leads to selection rules for reactions identical to the Woodward Hoffmann rules (for thermal reactions) analysis provides a very simple orbital. This OPCP does not need symmetry. One can do virtual reactions of one pair at a time to analyze the phases and derive the selection rule.