Dissecting reaction mechanisms

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Current Topics in Theoretical Chemistry
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The master plan

The master plan

- Introduction

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- Introduction
- I say some weird things

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- Applause

Outline

IUPAC Definitions

A word of advice from Roald Hoffmann

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My advice is: Push the concept to its limits. Be aware of the different experimental and theoretical measures out there. Accept that (at the limits) a bond will be a bond by some criteria, maybe not others, respect chemical tradition, relax, and instead of wringing your hands about how terrible it is that this concept cannot be unambiguously defined, have fun with the fuzzy richness of the idea.

IUPAC Definitions

Reaction mechanism

Reaction mechanism

"A detailed description of the process leading from the reactants to the products of a reaction, including a characterization as complete as possible of the composition, structure, energy and other properties of reaction intermediates, products and transition states."

"Inferences concerning the electronic motions which dynamically interconvert successive species along the reaction path (as represented by curved arrows, for example) are often included in the description of a mechanism. It should be noted that for many reactions all this information is not available and the suggested mechanism is based on incomplete experimental data. "

IUPAC Definitions

Primitive changes

Primitive changes

"One of the conceptually simpler molecular changes into which an elementary reaction can be notionally dissected. Such changes include bond rupture, bond formation, internal rotation, change of bond length or bond angle, bond migration, redistribution of charge, etc. The concept of primitive changes is helpful in the detailed verbal description of elementary reactions, but a primitive change does not represent a process that is by itself necessarily observable as a component of an elementary reaction."

IUPAC Definitions

Transition state

Transition state

"In the formalism of transition state theory the transition state of an elementary reaction is that set of states (each characterized by its own geometry and energy) in which an assembly of atoms, when randomly placed there, would have an equal probability of forming the reactants or of forming the products of that elementary reaction. "

IUPAC Definitions

Intrinsic reaction coordinate

Intrinsic reaction coordinate

"A minimum-energy reaction path on a potential energy surface in mass–weighted coordinates, connecting reactants to products via the transition state."

IUPAC Definitions

Concerted reaction

Concerted reaction

"Two or more primitive changes are said to be concerted if they occur within the same elementary reaction. Such changes will normally (though perhaps not inevitably) be energetically coupled. (In the present context, energetically coupled means that the simultaneous progress of the primitive changes involves a transition state of lower energy than that for their successive occurrence.) In a concerted process the primitive changes may be synchronous or asynchronous"

IUPAC Definitions

Synchronicity

Synchronicity

"A concerted process in which the primitive changes concerned (generally bond rupture and bond formation) have progressed to the same extent at the transition state is said to be synchronous."

The IRC

Toy system

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A well known S_N2 reaction

$$Cl^- + CH_2FCl \longrightarrow CH_2FCl + Cl^-$$

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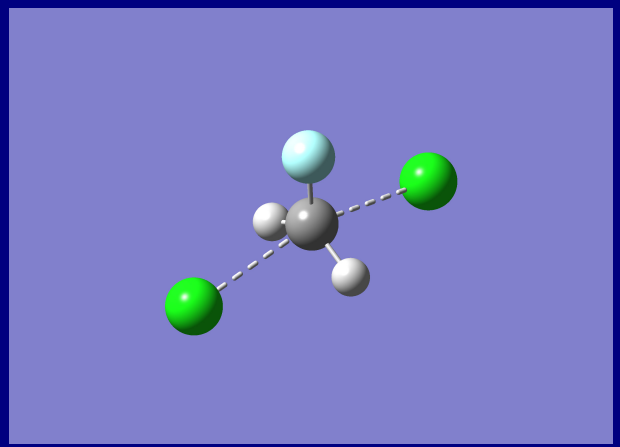

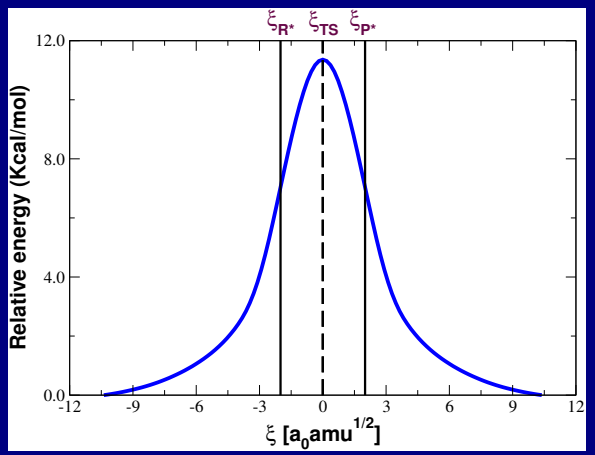

The IRC

The IRC

Our hypothesis

The IRC: Our hypothesis

The progress of a chemical reaction may be followed by monitoring changes in quantities that evolve in a (possibly) continuous fashion along the IRC

The IRC

Ask the oracle

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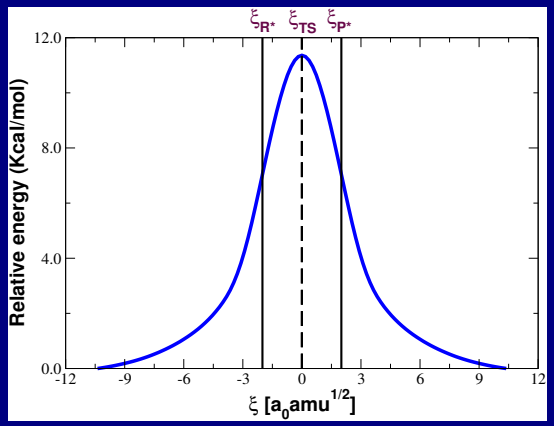

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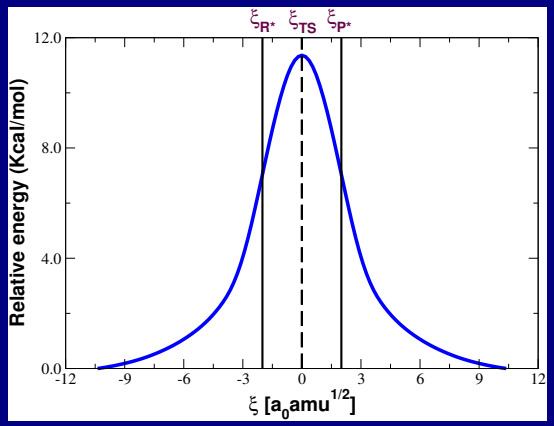

"He must be very ignorant for he answers every question he is asked" – Voltaire's Candide

The IRC

Dissecting the IRC

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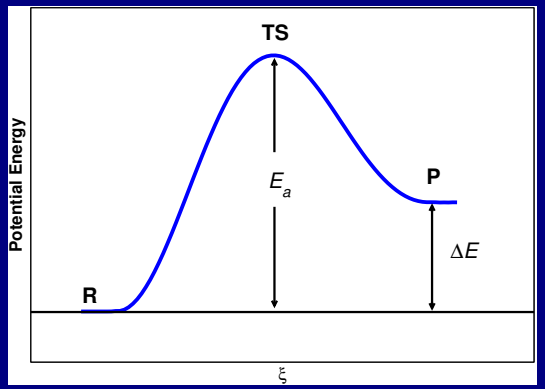
Reaction force, Reaction force constant

IRC, Reaction force



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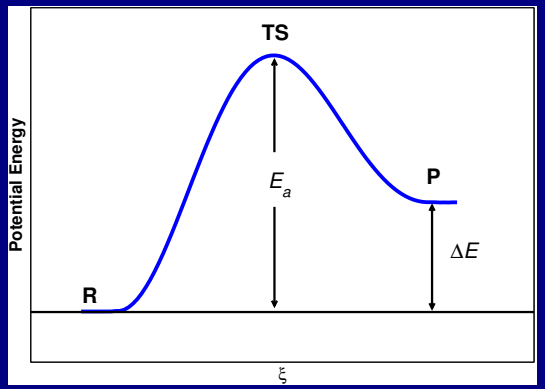

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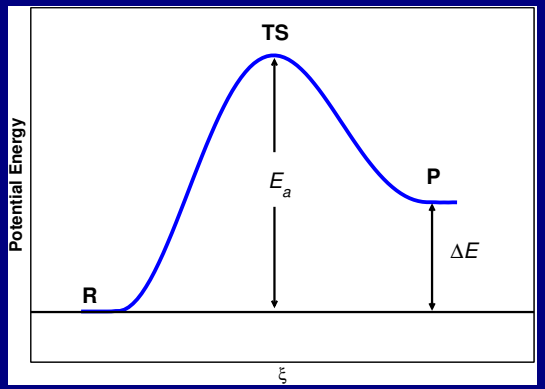

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The reaction force constant is obtained as

$$\kappa(\xi) = -\frac{dF}{d\xi} = \frac{d^2V}{d\xi^2}$$

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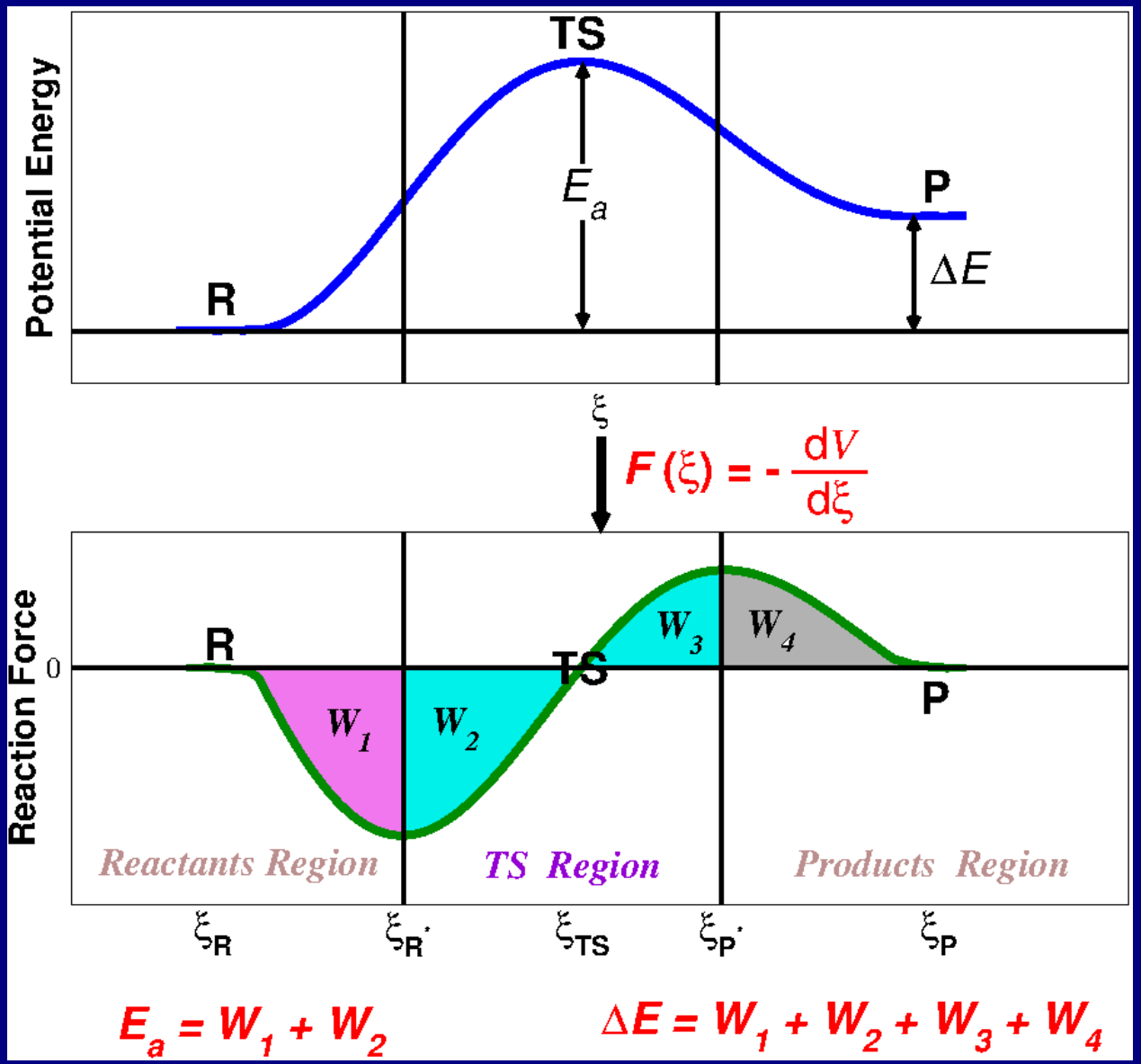

Dissecting the IRC

Evolution of bonding

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Reaction electron flux (REF)

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Synchronicity

The Michael reaction

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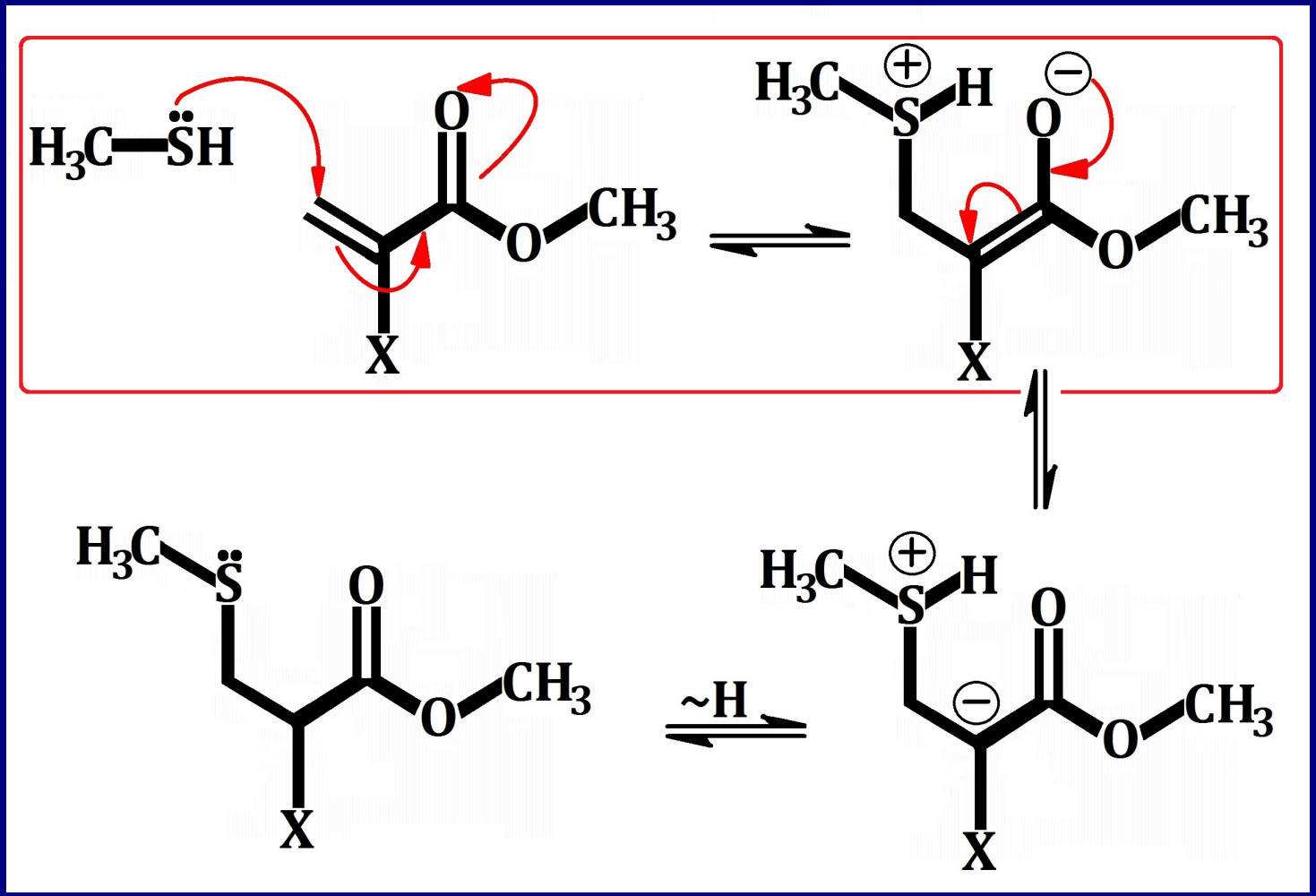

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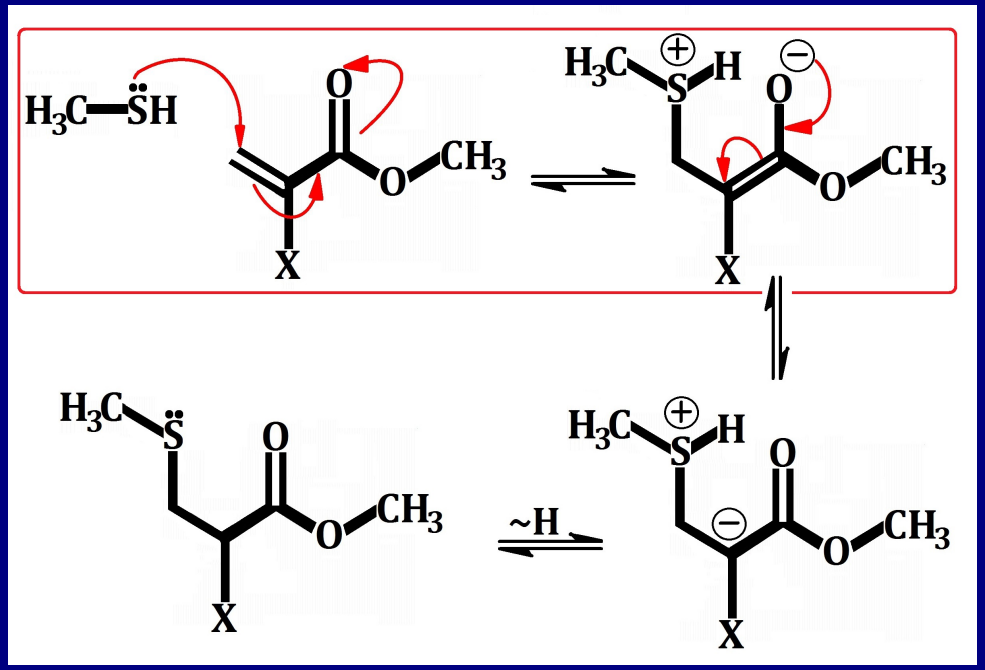
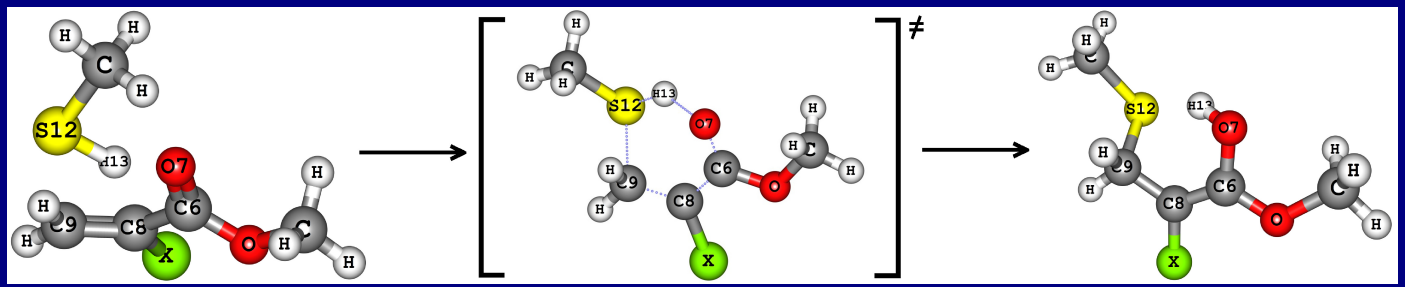
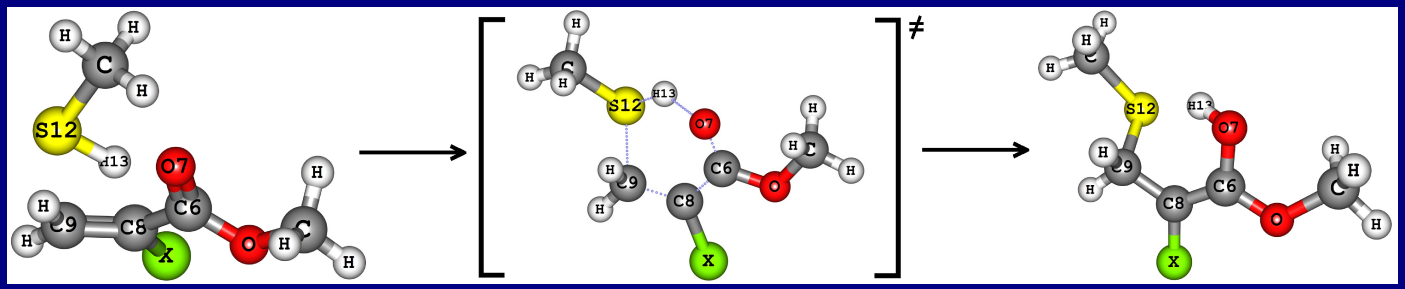




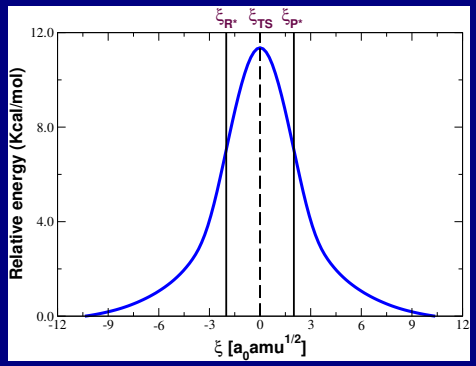
X = –F, –Me, –Cl, –H, –CN, –NO_2

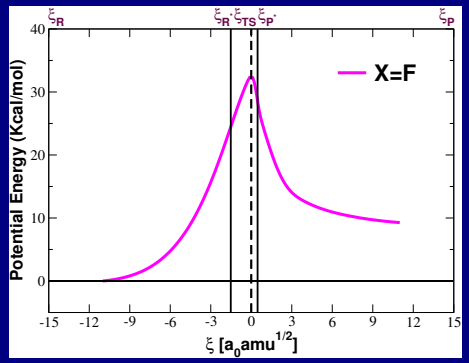
The Michael reaction: bond inventory

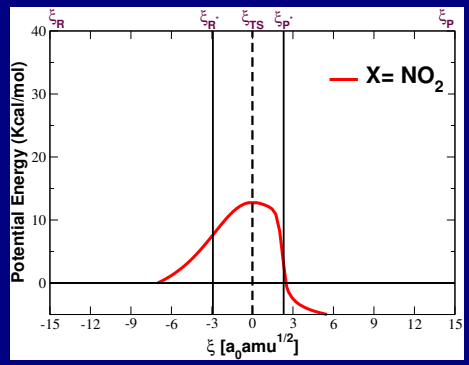


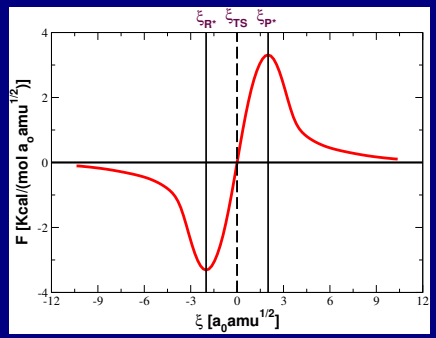
- S12–C9, O7–H13 are formed
- C6–C8 changes from single to double
- C8–C9, C6–O7 change from double to single
- S12–H13 is broken

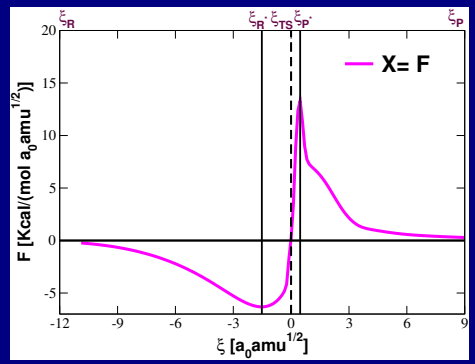
IRC, reaction force, reaction force constant

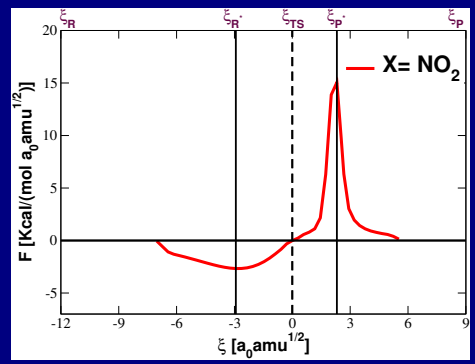


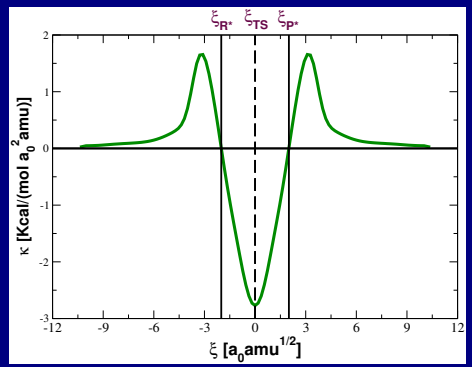


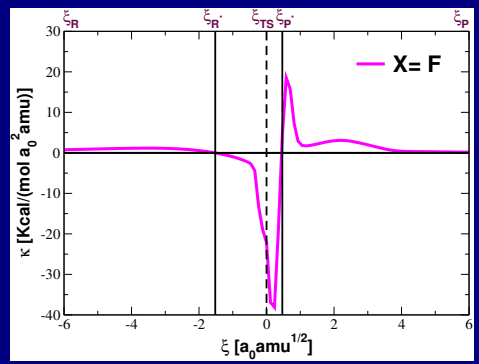


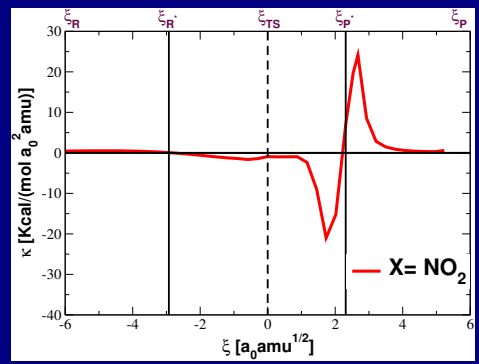




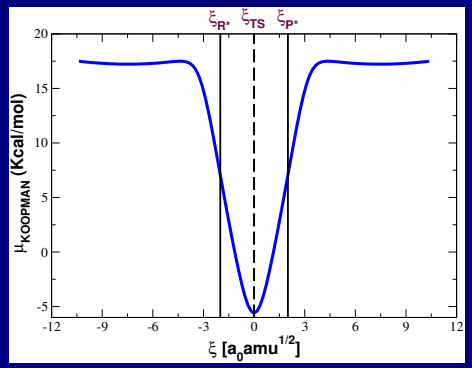


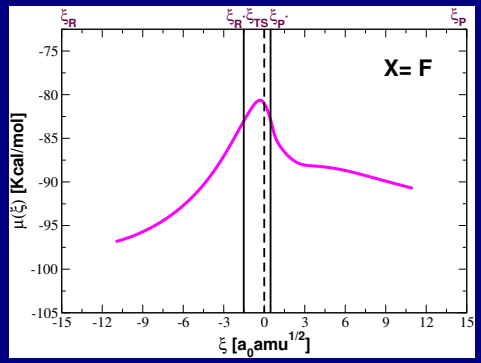


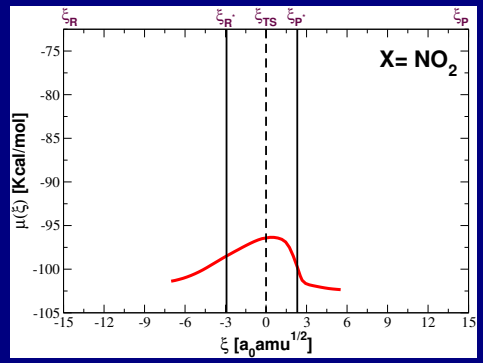


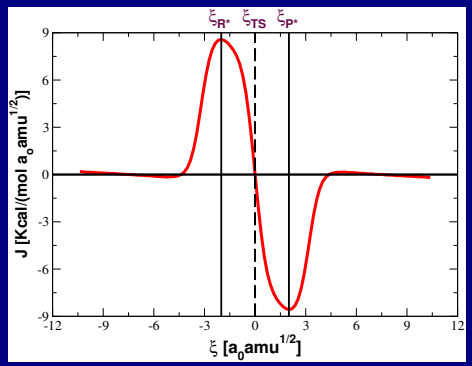


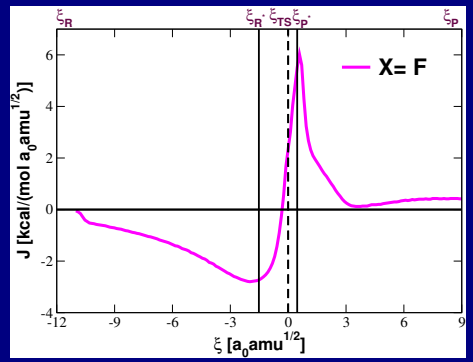
Chemical potential, REF

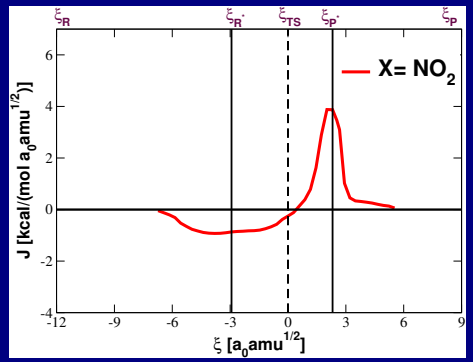




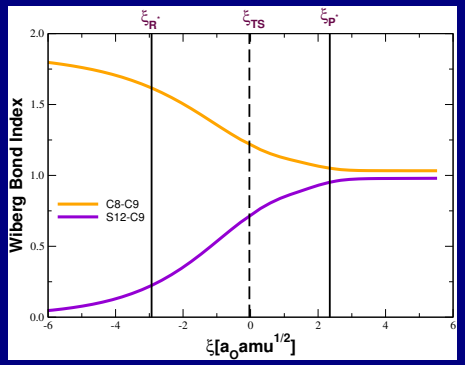


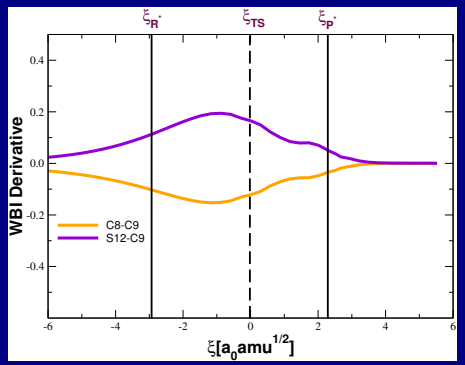


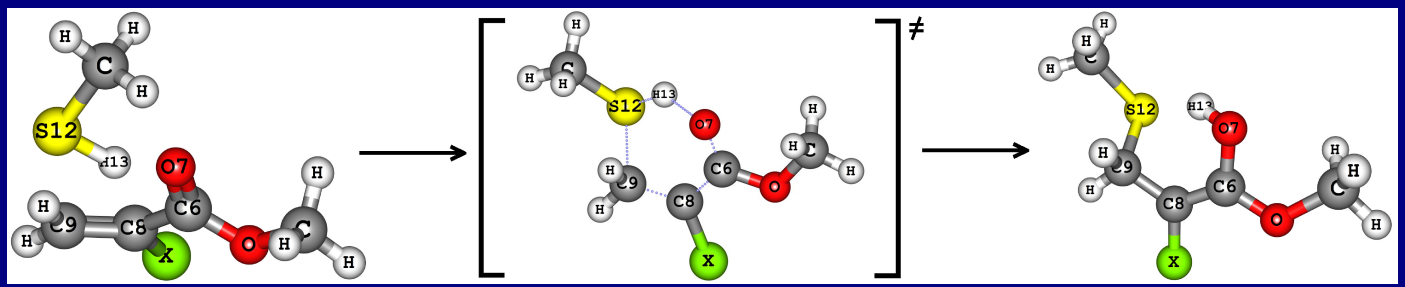




Bond orders and their derivatives







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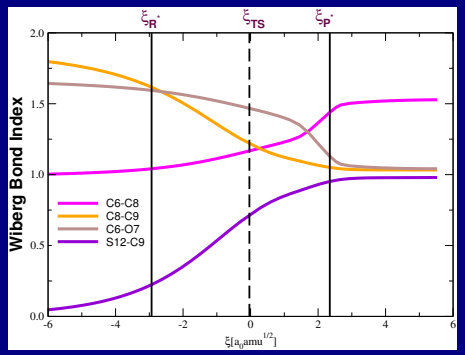

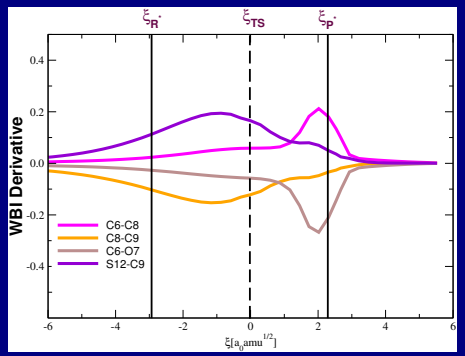

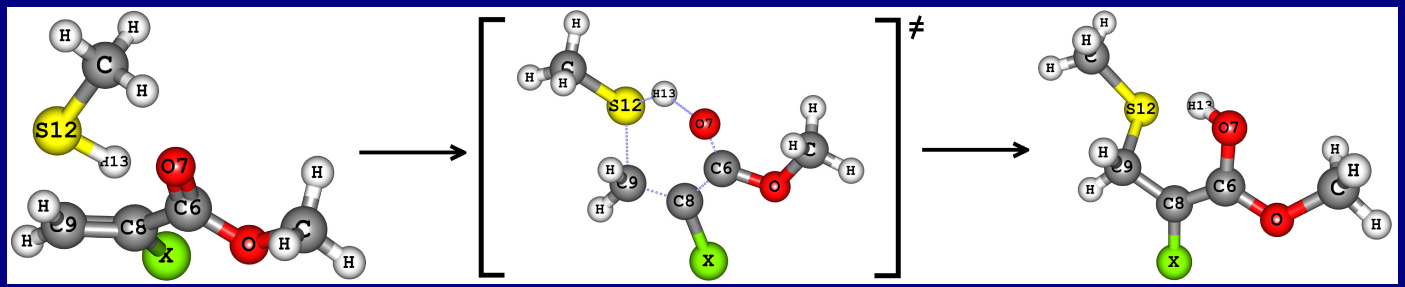

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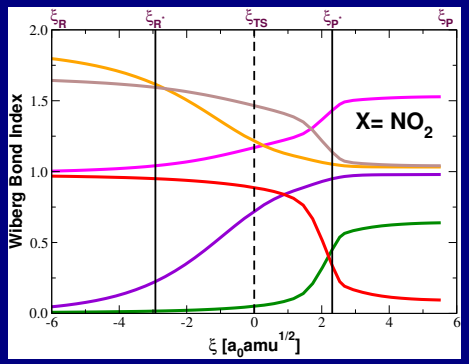

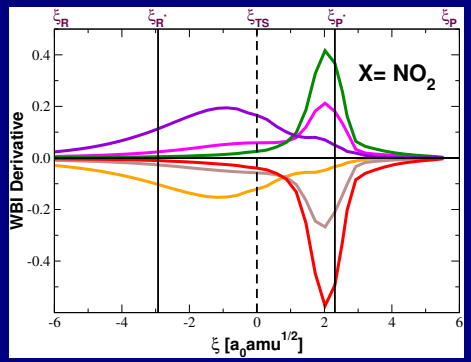

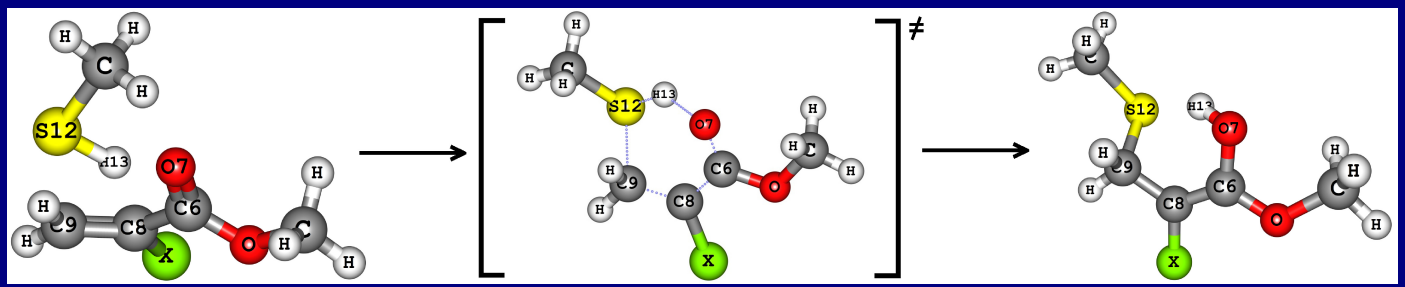

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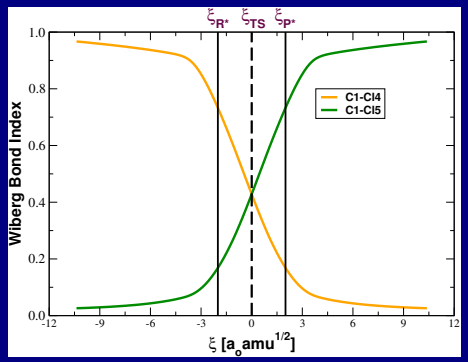
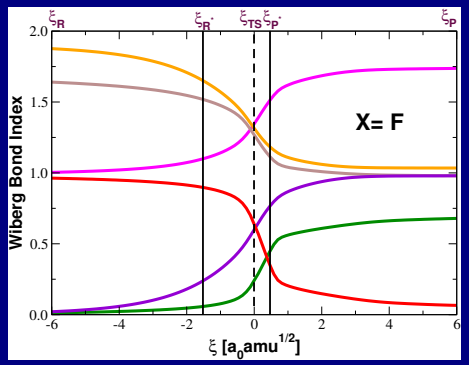
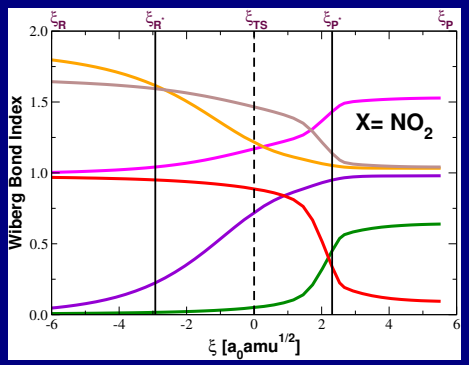
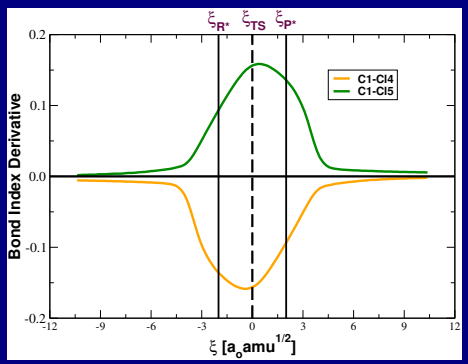
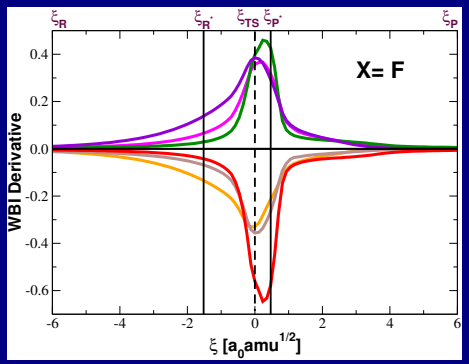
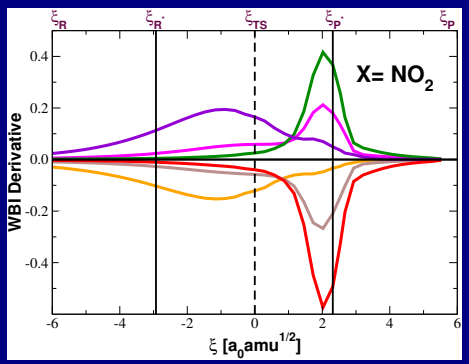


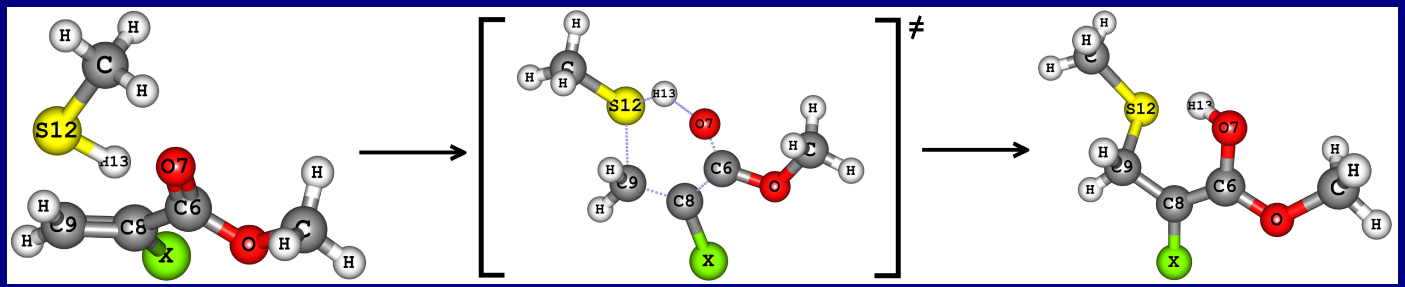






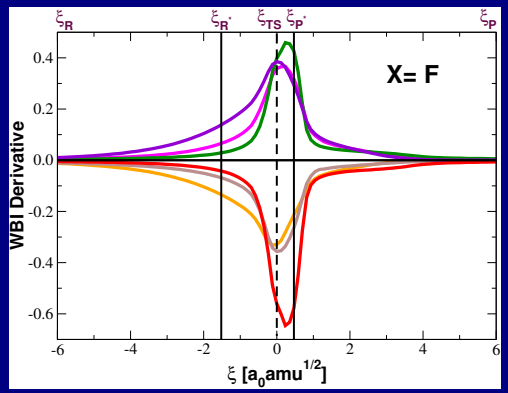






Synchronicity: Michael reaction

Activation energies in kcal/mol



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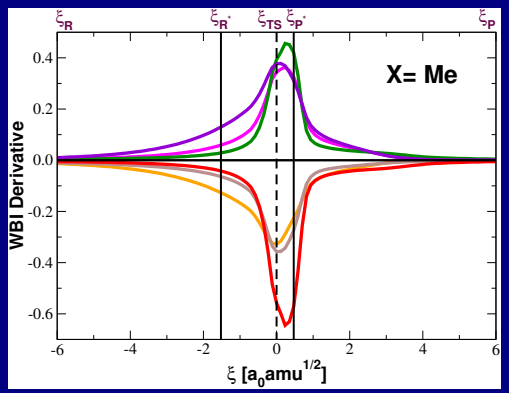

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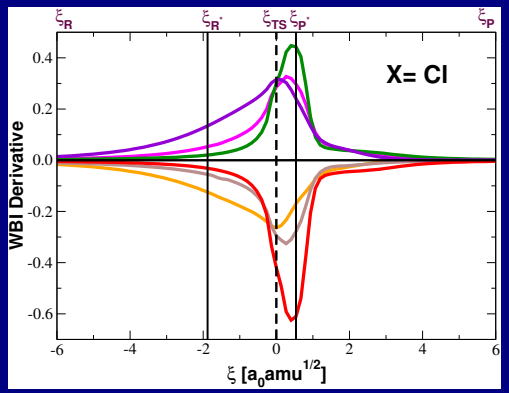

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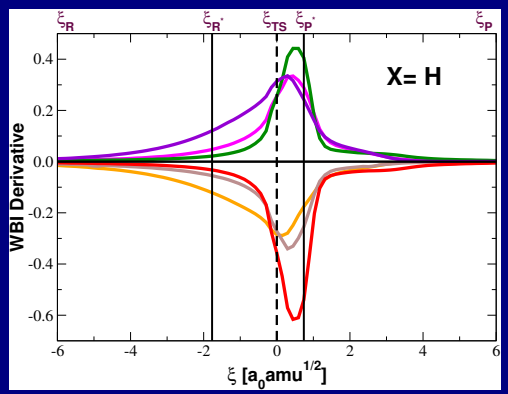

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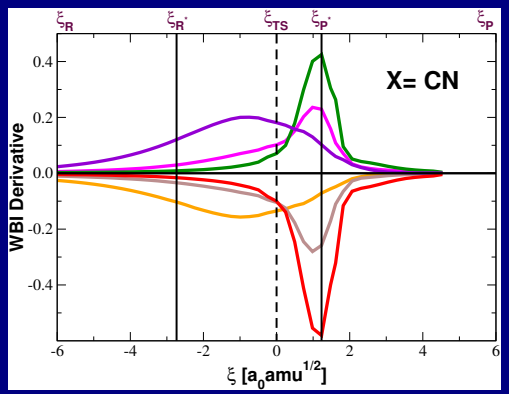

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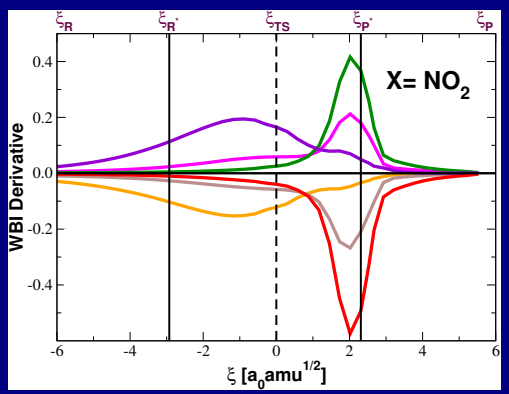
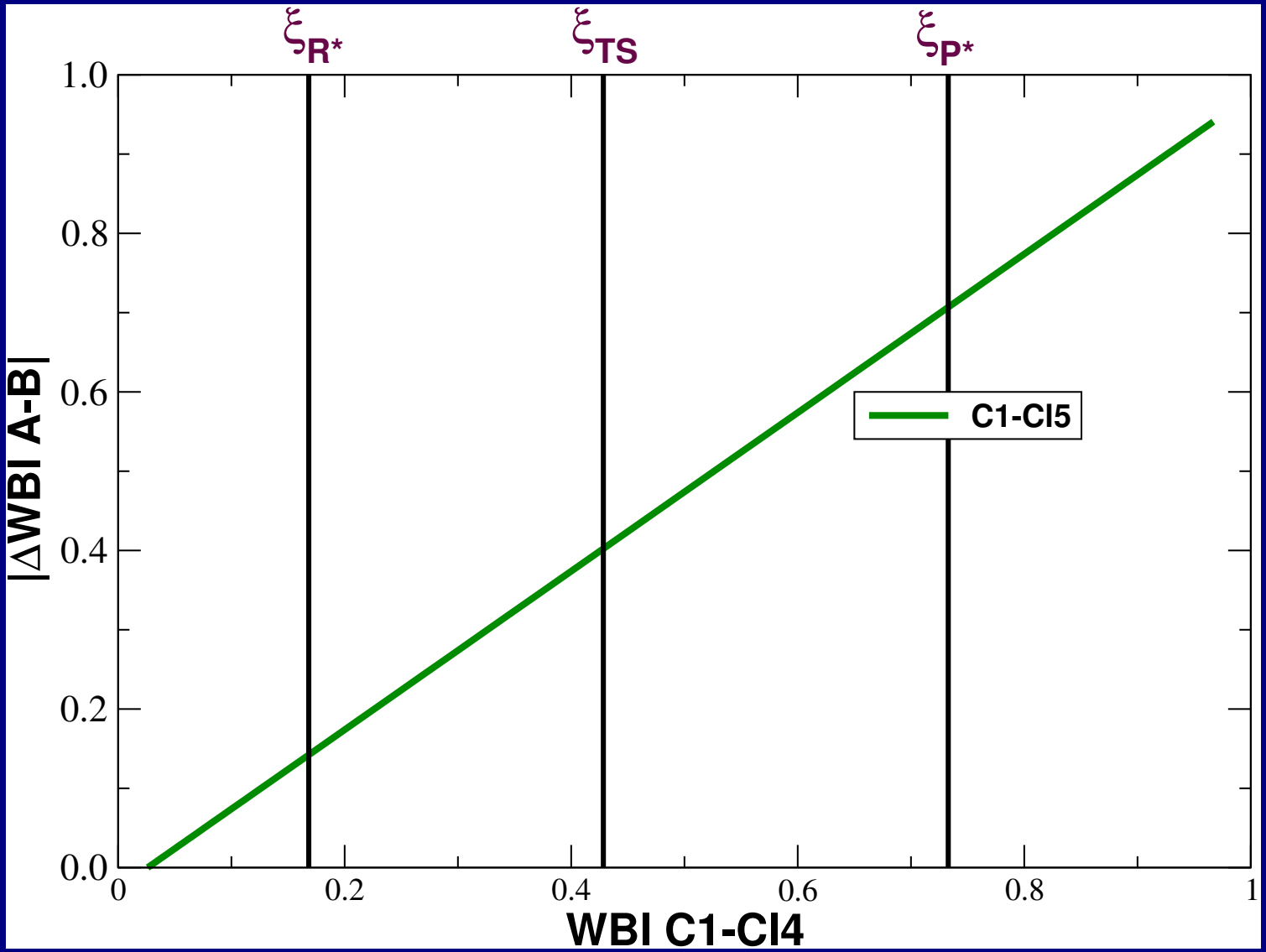


12.44

Synchronicity: our toy model



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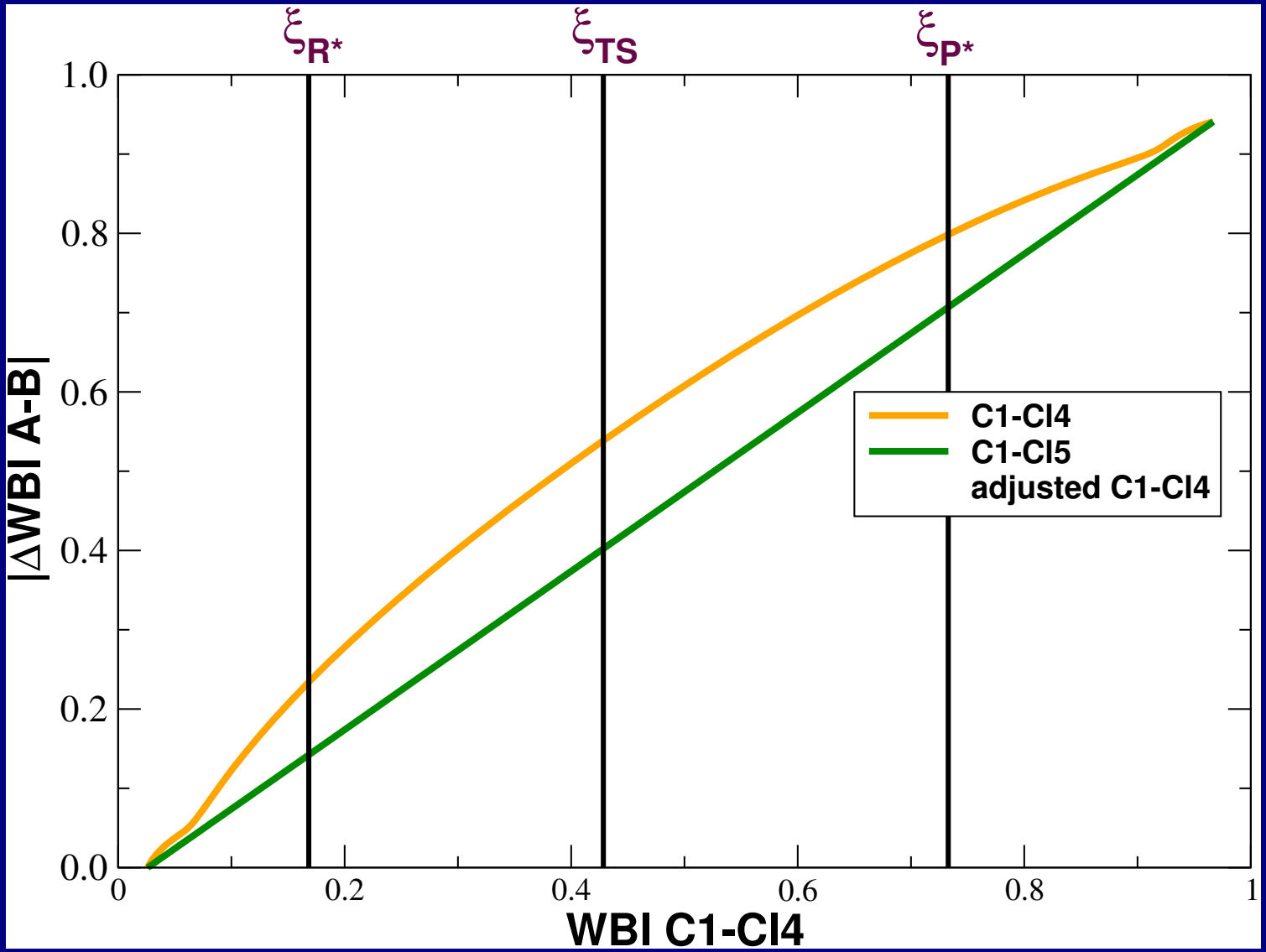
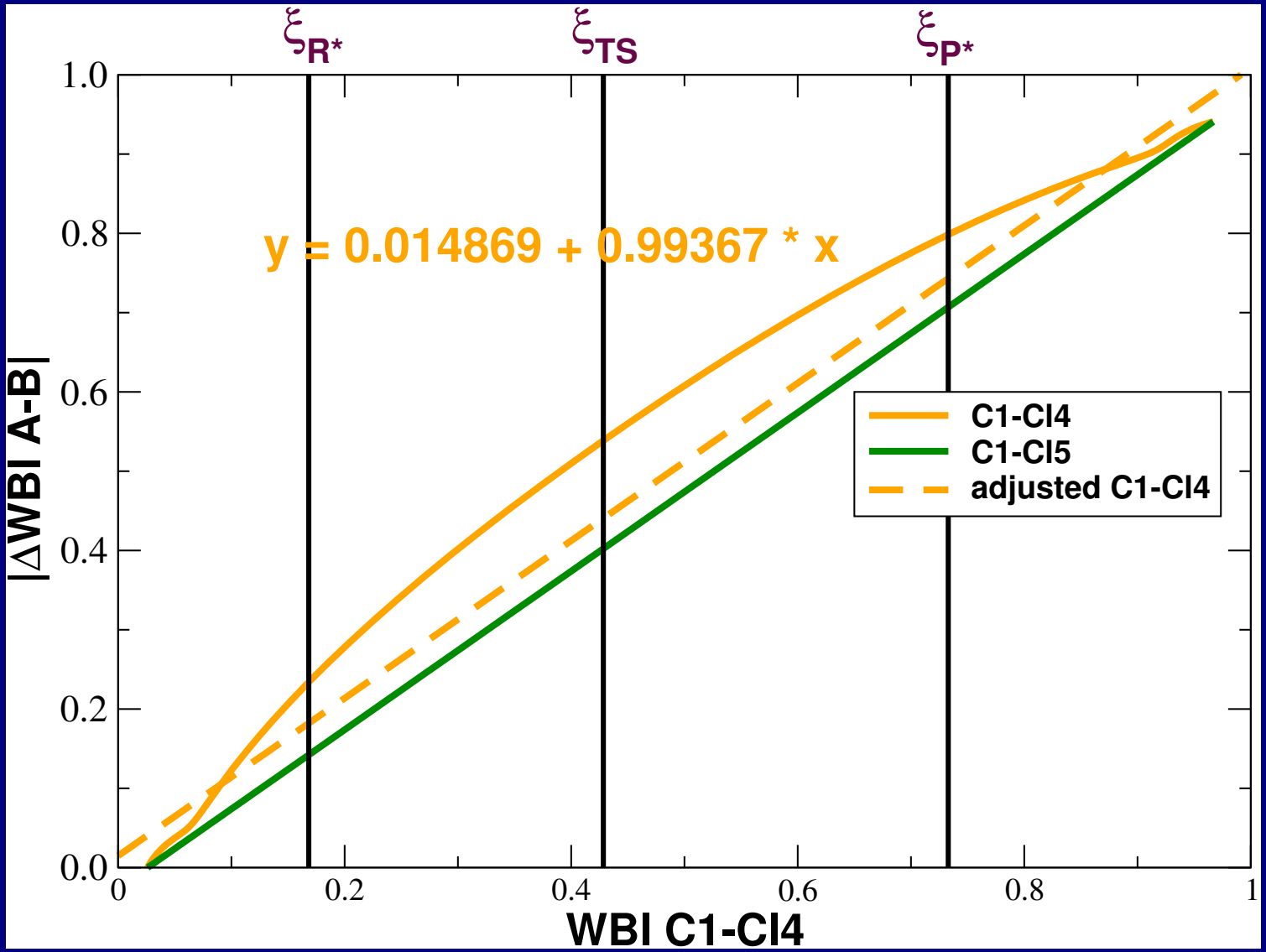
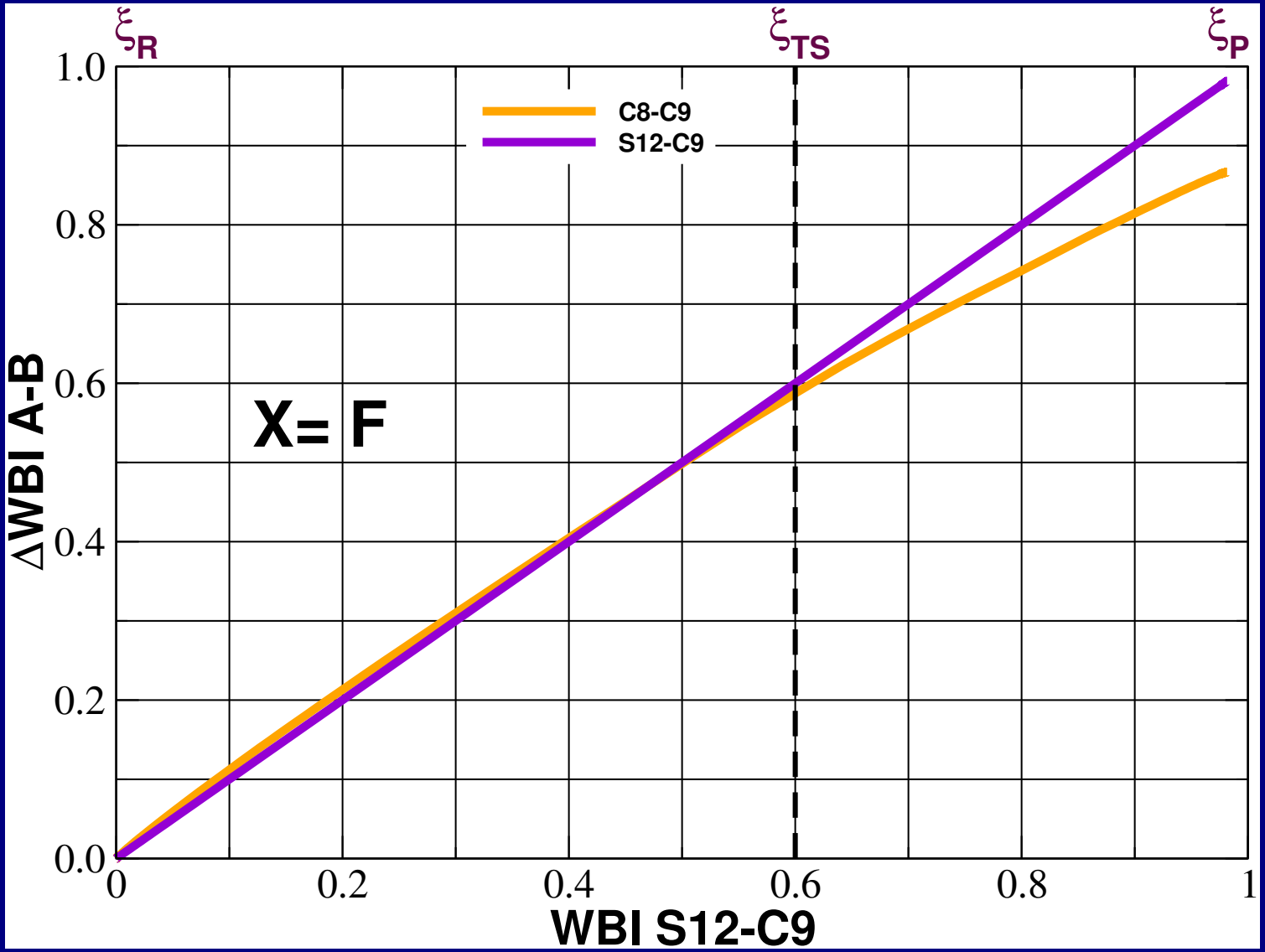


Synchronicity: our toy model



Synchronicity: Michael reaction



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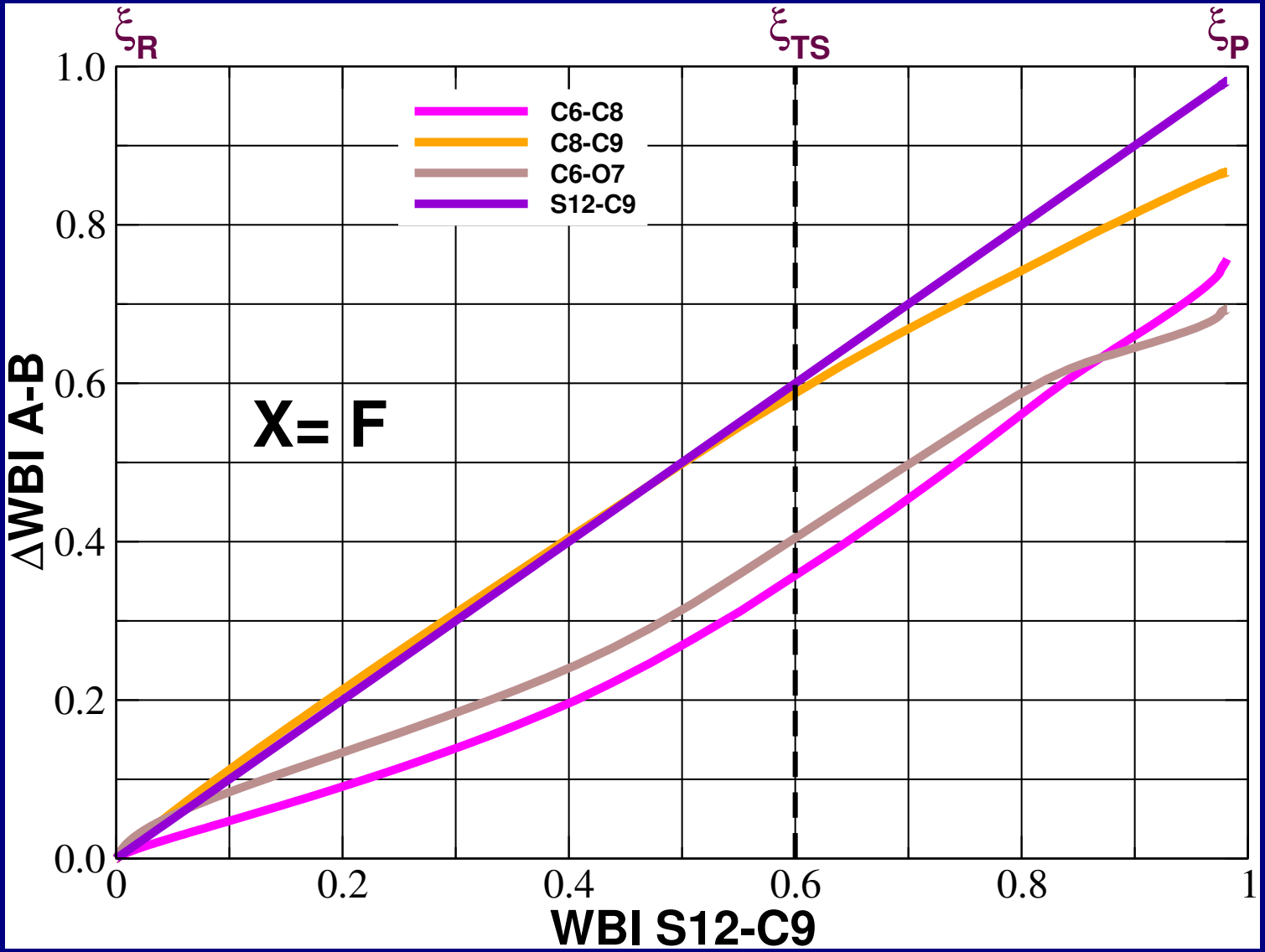

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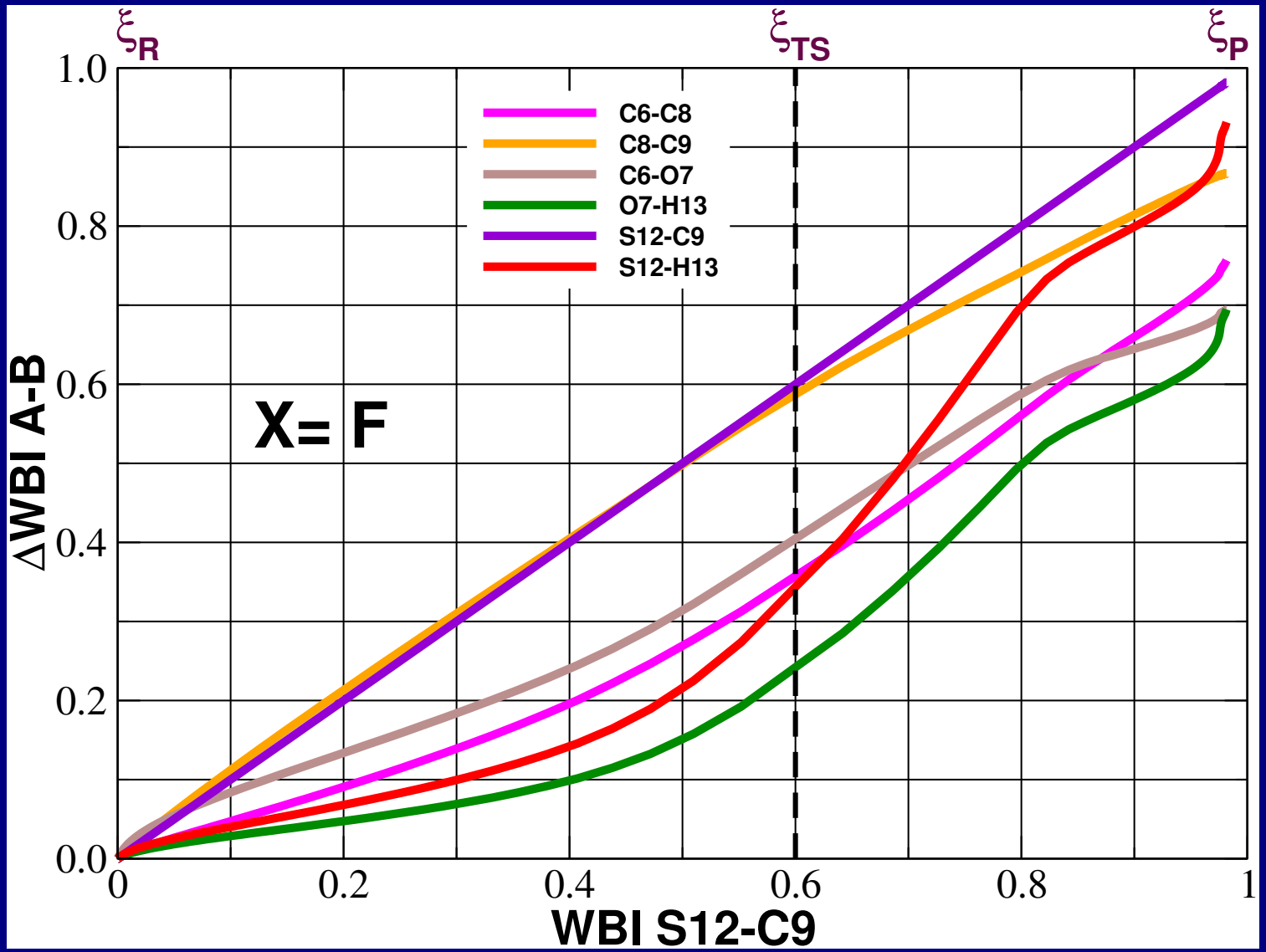

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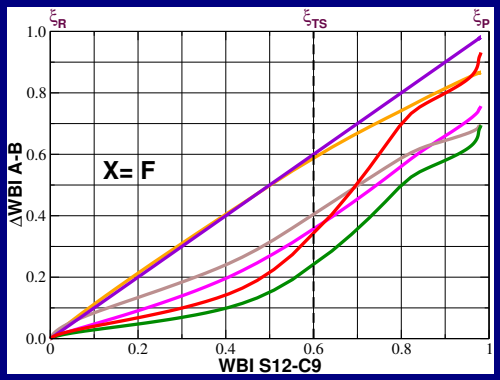

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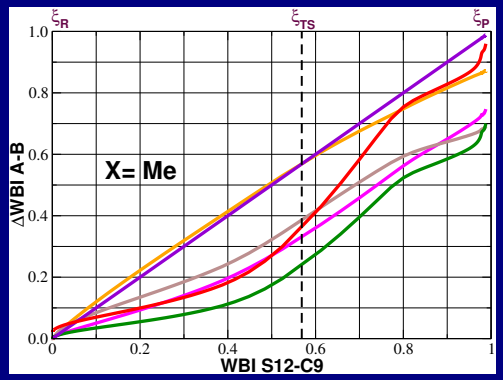

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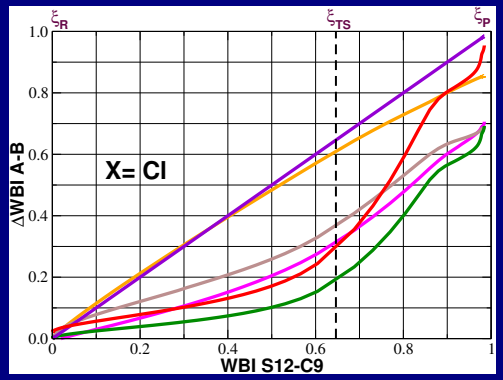

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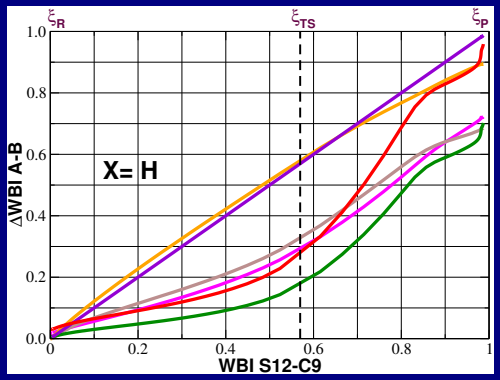

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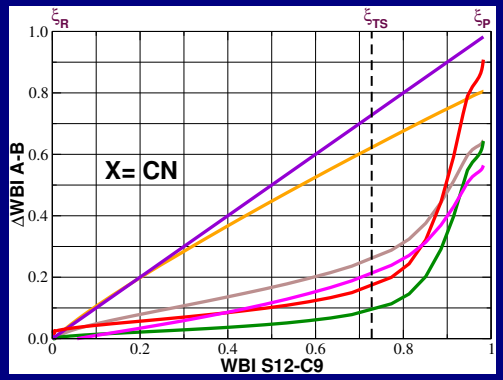

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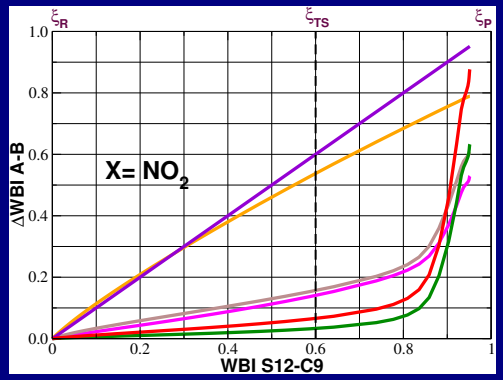

12.44

Final remarks

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Nucleophilic addition can be described as a highly non–synchronous process, during which, for all bonds involved, bond breaking/forming evolve at different rates. The mechanism can be described as a series of events in which the S$\cdots$C bond defines the interaction between the reactants and the progress of the chemical transformation.

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We postulate that highly complex chemical reactions that involve several primitive changes, lower their activation energies by favoring non–synchronicity.

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