Supramolecular Photochemistry

Cage and Conformational effects

Supramolecular Containers as Reaction Vessels



Cyclodextrins



Cucurbiturils



Pd Nano Cage





SDS / CTAC





Dendrimers NaCh / NaDCh





Octa acid











Zeolites

 \checkmark hydrophobic functionality \bigcirc \Rightarrow hydrophilic functionality

Water soluble polymer

Crystals

Supramolecular Containers





Soft reaction cavity e.g., solvent, micelles, liquid crystals,vesicles Moderately soft reaction cavity e.g., cyclodextrins, cucurbiturils, Rigid reaction cavity e.g., crystals, zeolites, capsules

Role of Free Space: Product Must Fit the Reaction Cavity







Conformational Control and Rotational Restriction



Energy diagram representation of supramolecular control of a reaction



An exemplar of supramolecular control of a photoreaction with two competing paths



Photochemistry of dibenzyl ketone as an exemplar of cage effect



Definition of cage effect



Cage effect (%) = $\frac{[AB] - ([AA] + [BB])}{([AB] + [AB] + [BB])} \times 100$







In micellar solutions the % cage depends on the surfactant concentration

Cage effect dramatically increases at a certain concentration of surfactant



For a given micelle (SDS) the exit rate gets slower as the hydrophobicity increases



Cage effect depends on the micellar exit rate: micellar size and hydrophobicity of the guest.

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EXIT RATE CONSTANT OF RADICALS FROM MICELLES



Micelle SDeS (C10) SDS (C12) STS (C14) SDS SDS SDS SDS SDS

For a given guest the rate of exit decreases with increasing micelle size.

For a given guest the rate of exit decreases with the hydrophobicity of the guest.

In micellar solutions the % cage depends on the hydrophobicity of the guest



Cage Effect

In micellar solutions the % cage depends on the the cage size



Sulfate surfactants $CH_3(CH_2)_nOSO_3Na$

Reactive radicals escape from smaller cages more easily.

Bigger micelles, more hydrophobic cage, slower exit to water

Understanding nuclear isotope effect





Vector representation of triplet-singlet conversions: intersystem crossing (ISC)



Intersystem Crossing in Radical Pairs



Vector representation of triplet-singlet conversions in I(RP) and I(BR): intersystem crossing (ISC)



Mechanisms of crossing from T to S (intersystem crossing, ISC)



Cage effect and nuclear isotope effect



Cage effect and nuclear isotope effect





Cage effect can be utilized for isotope enrichment



The competion is between cage escape and hyperfine induced ISC

Effect of an applied magnetic field on the T splitting



T levels split apart, T_0 has the same energy as S

Only $T_0 \rightarrow S$ ISC allowed

When H = O (The earth's magnetic field)



The effect of electron-nuclear hyperfine coupling on T-S conversion



Triplets coupled to nuclei with spin will cross to the singlets faster than triplets coupled to nuclei without spins.

Triplet radical pairs coupled to ¹³C will cross to singlets faster than triplets coupled to ¹²C

Result: Separation of ¹³C radical pairs from ¹²C radical pairs

The effect of external magnetic field on the cage effect

Ketone	Cage Effect at 0 G	Cage Effect at 13,000 G
	31	16
✓ ¹³ CH ₂ −C− ¹³ CH ₂ − DBK-2,2′- ¹³ C	46	22
$H_3C - CH_2 - CH_2 - CH_2 - CH_3$	59	31
4,4'Di-MeDBK		
	95	76
4,4'Di-t-BuDBK		

The cage effect decreases. More exit from host cage.

Isotope enrichment decreases in presence of applied magnetic field



Octaacid as a reaction cavity





The primary radical pair prefers to rotate than decarbonylate







Structure of MFI zeolites



Molecular vs. supramolecular radical-radical combination





(A) Model for pACOB Photolysis on MFI Zeolites



(B) Models for oACOB Photolysis on MFI Zeolites (Ketones in holes, left. Ketones on surface, right)



para ketone fits into the internal surface

Ketone completely inside: 100 % cage !







|≺ → →| 5.3 Å × 13.3 Å



ortho ketone does not fit into the internal surface

Ketone half inside, half outside: -100 % cage !!



Photodecarbonylation of ketones in crystalline state

Requirements

- The compound must be and stay crystalline.
- Crystals must not melt (solid-solid reactions must occur below eutectic point).
- \clubsuit Presence of suitable radical stabilizing substituents at α and α' carbons.
- The ketones must have high triplet yields and triplet energies.

Advantageous

- * Occurrence of reaction within crystal boundaries Selective and specific.
- ✤ Solvent free.







Reactions in crystals are highly efficient, selective and general



Solid State vs Solution Photodecarbonylation

Remarkable control exerted by crystals holds the radical pair from diffusing apart.





5 steps including a solid state photoreaction ~ 60% total yield.

An schematic of supramolecular conformational control of a photoreaction with two competing paths: $*R \rightarrow I(BR) + *R \rightarrow I(RP)$



Controlling the competition between Type I and Type II products by controlling the $R \rightarrow I(BR)$ of the Type II process



(b) Supramolecular inhbition of Type II reaction



Type II Inhibited by preorganization

Conformational Control and Rotational Restriction







- $\mathbf{a} = -CH_3$
- $\mathbf{b} = -\mathbf{C}_2\mathbf{H}_5$
- $\mathbf{c} = n C_3 H_7$
- $\mathbf{d} = n C_4 H_9$
- $e = n C_5 H_{11}$
- $f = n C_6 H_{13}$
- $g = n C_7 H_{15}$
- **h** = $n C_8 H_{17}$



Supramolecular mechanistic rationalization of the micellar effect: Preorganization of the conformation of *R



Exemplar of micellar control of ratio of Type I and Type products



