Catalytic Solar Water Splitting Inspired by Photosynthesis. Homogeneous Catalysts with a Mechanical ("Machine-Like") Action

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Sub-theme: Molecular Machines

- Much interest in developing "molecular machines" that drive chemical reactions

- But, what is the "mechanical action" that must occur within a molecular catalyst to turn it into a molecular machine?
Two General Methods of Inducing Change

- **Energy Gradient** ("Thermodynamics")
  
  Change driven by an overall release of energy

  e.g. a ball falling to Earth under gravity

- **Mechanical Interaction** ("Mechanics")
  
  Change driven by a physical collision (action-reaction sequence that plays out over time)

  e.g. two billiard balls physically colliding
**Chemistry: Collision Theory**

**STEP (1)**
Reactant collision controlled by the "collision frequency" (A)

**STEP (2)**
Product formation controlled by the "activation energy" (Eₐ)

"Mechanical" reaction:
\[ H^+ + OH^- \rightarrow H₂O \quad k = 10^{-10} \text{ s} \]
What Happens in Catalysis?

**STEP (1)**
Reactant collision controlled by the "collision frequency" \( (A) \)

**STEP (2)**
Product formation controlled by the "activation energy" \( (E_a) \)

- **Reactants**
- **Catalyst** binds & activates reactants
- **Transition state** formed
- **Products** bind catalyst and are released

Potential Energy vs Reaction Coordinate graph:
- **Uncatalyzed**
- **Catalyzed**
- **Reactants**
- **Products**
“Mechanical” Catalysts: H₂ generation

Dynamic proton binding

Two dynamic processes (catalyst flexing and proton binding) which are only synchronized if the catalyst flexes rapidly about a structure that complements the transition state

produces 5 molecules H₂ s⁻¹ catalyst⁻¹ over at least 5 days of continuous operation

Chem Commun 2004, 308
Chem Eur J 2009, 15, 4746
“Mechanical” Catalysts: \( \text{O}_2 \) reduction

\[
\begin{align*}
\text{O}_2 & \quad \xrightarrow{3} \quad \text{H}_2\text{O} \quad (4 \text{ e}^- \text{ process}) \\
\text{O}_2 & \quad \xrightarrow{4} \quad \text{H}_2\text{O} \quad (4 \text{ e}^- \text{ process})
\end{align*}
\]

“Pac-Man” Catalyst

*Chem Commun* **2007**, *3352*
*Chem Eur J* **2009**, *15*, *4746*
Some Common Features of “Mechanical” Molecular Catalysts

(1) Reaction controlled by the *Catalyst-Mediated Collision Frequency* (low *Activation Energy*)

(2) The maximum catalytic rate depends on the rate of conformational flexing (conformational flexing = the “mechanical impetus”)

(3) Catalyst typically flexes rapidly about a shape that *complements the transition state*

(4) Highly efficient and selective form of catalysis (like a machine)

(5) Michaelis-Menten kinetics

*Chem Eur J* **2009**, *15*, 4746

• *These features also found in many enzymes*

QUESTION: Are enzymes mechanical catalysts?
Mechanical Catalysis: Methods of Enzymatic, Homogeneous, and Heterogeneous Catalysis
Swiegers, G. F.
Can we Mimic an Enzyme?

Water-Oxidizing Complex of Photosystem II (PSII-WOC)

Bio-inspired Mn-oxo Cubane Model Complex
G. C. Dismukes, Princeton University

Cubane:
- Shape and structure similar to enzyme active site
- Dynamically self-assembles
- Flexible
- Low activation energy for O₂ release (photolytic)
Cubane forms $O_2$ when illuminated

\[ \text{hv} \]

+ 1 ligand released

Mn-Mn distance lengthens

O-O distances shorten

Corner O's collide

Peroxo ($O_2^2-$) forms

Superoxo ($O_2^-$) forms

"butterfly" $+ O_2$

DeAngelis, Carr
Cubane in Nafion layer on GC electrode

Electrode biased at 1.0 V (vs. Ag/AgCl)

Illuminated at 250-750 nm

Peak turnover frequency:
270 molecules O₂ h⁻¹ catalyst⁻¹

Total turnovers:
>1000 readily achieved

Angew Chem Int Ed Engl 2008, 47, 7335
Cubane$^+$ ion-exchanged into Nafion: CV
Catalyst dis-assembles and re-assembles under turnover conditions

Inorg Chem 2009, 48, 7269
CV

$\text{Ru(bpy)}_3^{2+} \xrightarrow{h\nu} \text{Ru(bpy)}_3^{3+} + e^-$

8+ in Nafion

Potential V (vs Ag/AgCl)

Current (µA)
Water-Splitting “Graetzel” Cell

L. Spiccia, Monash University
Water-Splitting “Graetzel” Cell

- System splits seawater into pure oxygen (no chlorine formation)
- Spin-off company: “Cube Catalytics LLC”
  (funded by New Energy Ventures, New Jersey)

Uses H₂O as electrolyte – even impure H₂O (seawater).
Eliminates the need for acetonitrile electrolyte which bedevils existing Graetzel cells

*J Am Chem Soc* 2010, 132, 2892
H₂O → [Mn₄O₄L₆]⁺ → O₂ + 4H⁺ → H₂O

Nafion
[Ru(bipy)₂(dcbipy)]²⁺
TiO₂ on FTO
External circuit

Photoanode

4e⁻

Tetra manganese cluster
Supporting amino acids
P₆₈₀
Phenophytin
Charge carriers: Qₐ etc.

PhotosystemII
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