Catalytic solar water splitting inspired by photosynthesis. homogeneous catalysts with a Mechanical ("Machine-like") action

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Abstract
Chemical reactions may be controlled by either: the minimum threshold energy that must be overcome during collisions between reactant molecules / atoms (the Activation Energy, $E_a$), or: the rate at which reactant collisions occur (the Collision Frequency, $A$) (for reactions with low $E_a$). Reactions of type (2) are governed by the physical, mechanical interaction of the reactants. Such mechanical processes are unusual, but not unknown in molecular catalysts. We examine the catalytic action and macroscopic properties of several abiological mechanical catalysts and show that they display distinct similarities to enzymes in general. An abiological model of the Photosystem II Water Oxidizing Complex that appears to employ a mechanical action has now been found to be a remarkably active and sustained molecular catalyst of water oxidation when illuminated by sunlight. A free-standing Dye-Sensitized Solar Cell that spontaneously splits water into hydrogen and oxygen has been developed using this catalyst.

Keywords
mechanical, machine, like, homogeneous, action, photosynthesis, inspired, splitting, water, solar, catalytic, catalysts

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

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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:

\[ \text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} \quad k = 10^{-10} \text{ s} \]
What Happens in Catalysis?

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

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

- **Mechanics**
  - Catalyst binds & activates reactants
  - Transition state formed
  - Products bind catalyst
  - Products released

- **Thermodynamics**
  - Energy: $E_a$
  - Reaction Coordinate

Potential Energy

- 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: $O_2$ reduction

O$_2$ $\rightarrow$ H$_2$O (4 e$^-$ process)

“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
Swiegors, 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

$\text{hv}$

$\text{Mn-Mn distance lengthens}$

$\text{O-O distances shorten}$

$\text{Corner O's collide}$

$\text{+ 1 ligand released}$

$\text{+ 1 ligand}$

$\text{+ 2 H}_2\text{O}$

$\text{- 4H}^+ - 4 \text{e}^-$

$\text{Peroxo (O}_2^{2-}\text{) forms}$

$\text{Superoxo (O}_2^-\text{) forms}$

$\text{"butterfly"}$

$\text{9} + \text{O}_2$

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 O$_2$ h$^{-1}$ catalyst$^{-1}$

Total turnovers:
>1000 readily achieved

Angew Chem Int Ed Engl 2008, 47, 7335
Cubane$^+$ ion-exchanged into Nafion: CV

Potential (V vs Ag/AgCl)

Current (µA)

8$^+$ in Nafion

Mn$^{2+}$ in Nafion
Proposed Mechanism

Catalyst dis-assembles and re-assembles under turnover conditions

Inorg Chem 2009, 48, 7269
CV

8+ in Nafion

\[
\text{Ru(bpy)}_3^{2+} \xrightarrow{h\nu} \text{Ru(bpy)}_3^{3+} + e^-
\]
Water-Splitting “Graetzel” Cell

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

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

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

$\text{H}_2\text{O}$ → $\text{H}_2\text{O}$

$\text{O}_2 + 4\text{H}^+$

$[\text{Mn}_4\text{O}_4\text{L}_6]^+$

Nafion

$[\text{Ru(bipy)}_2(\text{dcbipy})]^{2+}$

$\text{TiO}_2$ on FTO

External circuit

4e$^-$

Tetra manganese cluster

Supporting amino acids

P680

Phenophytin

Charge carriers: $Q_a$ etc.

Photoanode

PhotosystemII
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