Industrial Applications of Molecular Modeling

July 2000

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- **Pharmaceuticals & Food Additives**
  - **Merck – Merck Molecular Force Field for Aqueous Biomolecules**
  - **Nutrasweet – Rheology of Thickening Agents**
  - **Unilever – Copolymer Composition of Emulsifiers**
- **Commodity Chemical**
  - **Dow – Accurate Thermodynamic Data for Hazard Analysis**
  - **DuPont – From Process Design to Environmental Fate**
- **Petrochemical**
  - **Amoco – Thermodynamics of Intermediates in Design of Catalytic Cycle**
- **Automotive**
  - **Lubrizol – Isolating Effect of Individual Components of Complex Product Mixtures, Catalyst Substitution**
  - **Ford – Improved 3-Way Catalyst Design for Fuel Economy**
- **Coatings & Colors**
  - **PPG – Electronic Transitions to Design Photochromics**
  - **Eastman Kodak – Colors and Electrostatics for Imaging Systems, Acylation Process Improvement**

Merck – Thomas Halgren

More accurate Molecular Mechanics specific for biomolecules in aqueous environment: drug docking & design, protein folding, CoMFA (Comparative Field Analysis).

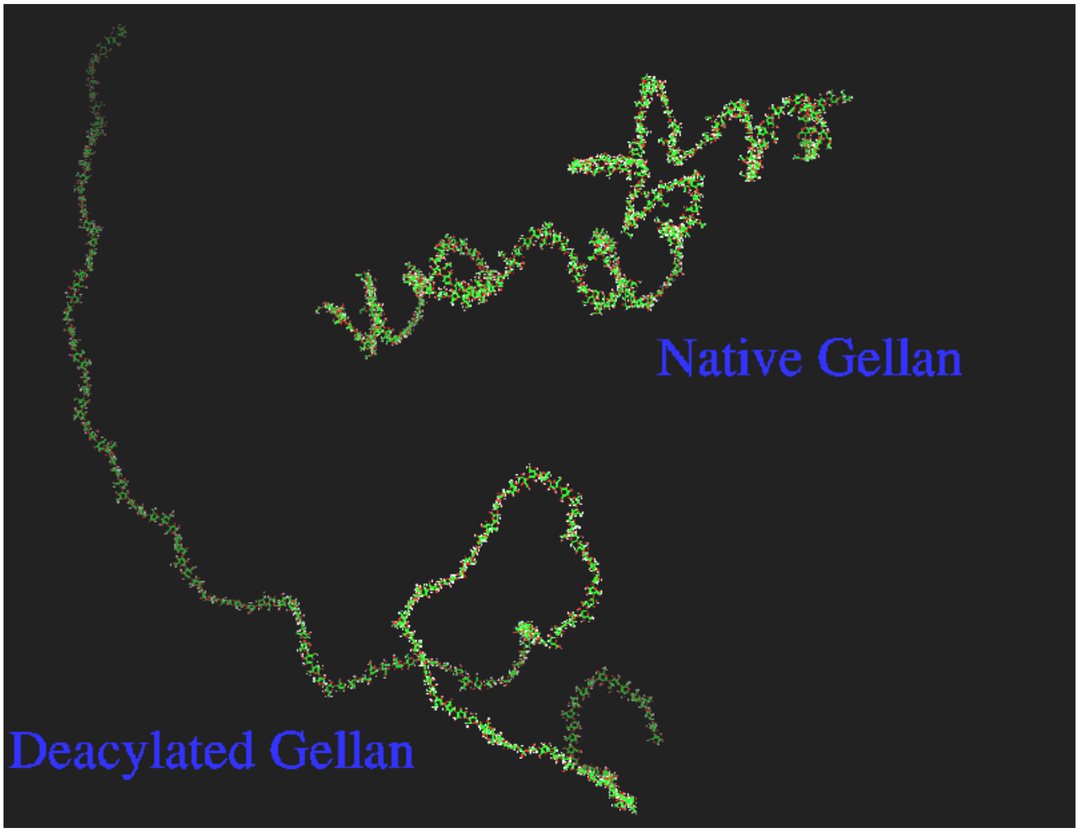
- **Merck Molecular Force Field (MMFF94)**
  - **Ab Initio (MP2/6-31G*) Derived Parameters**
  - **Class II Force Field**
    - **Quartic Term (correct for anharmonicity)**
    - **Cross Term (coupling of vibrations)**

- **Improved Energies**
  - **Better Conformational Barriers**
  - **Better Hydration of Ions (2.9 vs. 8.2 kcal w/ MM2)**

NutraSweet Kelco – Todd Telashek

Control rheology of acylated polysaccharide gelation agents used as thickening agents for food and other applications.

- **Model chain extension of chains with various levels of acylation by RIS-MC.**

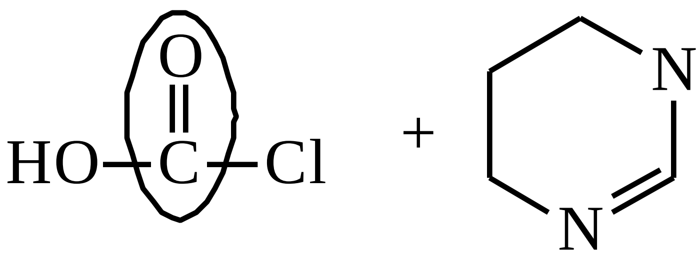


- **Trade off brittleness with extended chains at low acylation levels vs elasticity at high acylation levels.**

DOW – Nelson Rondan, David Frurip

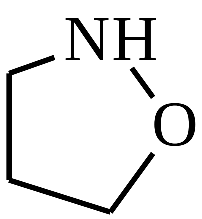
Indirect calculation of thermodynamics for hazard analysis and process design.

- **Larger Molecules than DuPont**
  Benson Group Contribution Method in CHETAH
- **High Level Ab Initio Calculations (G2) to Fill in Missing Groups**



25 Hrs. for MP4/6-311G**

- **Identified Explosion Hazard by Heat of Decomposition**



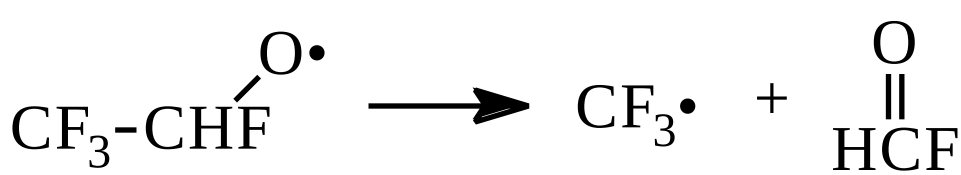
80% of TNT

DuPont – Dave Dixon

Direct calculation of accurate thermodynamics and kinetics for complete product cycle.

- **Grand Challenge – design chemical plant from scratch**
  - **Thermodynamics**
  - **Kinetics**
  - **Catalyst Design**
  - **Process Simulation**
  - **Fluid Dynamics**
  - **etc.**

- **CFC Alternatives – HFC-134A**
  - **Intermediates in Potential Process for CF_3CH_2F**
    - **NIST Measurement – $50K + 90 Days**
    - **MP2/TZP Calculation – $5k + 7 days**
  - **Predict Environmental Fate**
    - **Atmospheric Kinetics**



Amoco – Joe Golab

Find thermodynamic balance in design of catalytic cycle.

- **Upgrade Value of Natural Gas: CH_4**

$$CH_4 + O_2 \longrightarrow CH_3OH$$

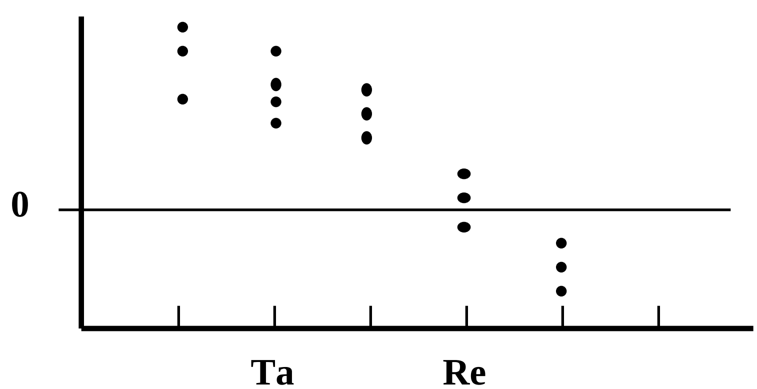
1st Step in Oxidative Coupling to Higher Hydrocarbons

- **Ta Oxides React with CH_4**

  Alkylates Oxide

  Doesn't Release Methanol

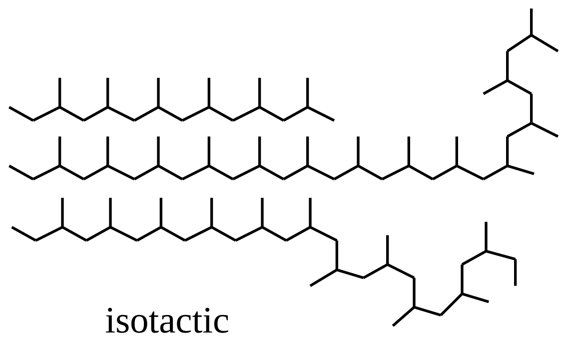
- **Model 3rd Row Transition Metal Oxide Families**
  Oxidation, Coordination, and Spin States
  ECP's for Relativistic Atoms
  Alkylation Thermodynamics
  Barrier to Methanol Dissociation



Petrochemical Companies – Bob Waymouth, Others

Design of new generation olefin polymerization catalysts: elastomeric PP by control of tacticity in blocks.

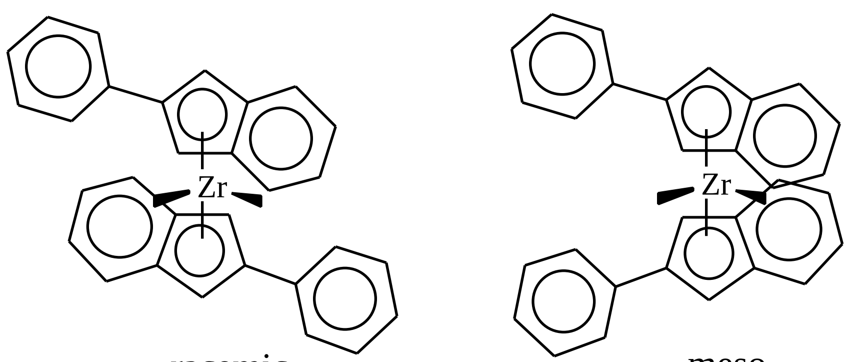
- **Physically Cross-linked Blocks**



isotactic crystalline   atactic amorphous

- **Model Multiple Forms of Single Site Catalyst**

  Relative Energies by DFT for Transition Metal



racemic   meso

Relative Run Lengths vs. Rate of Change in Catalyst Form

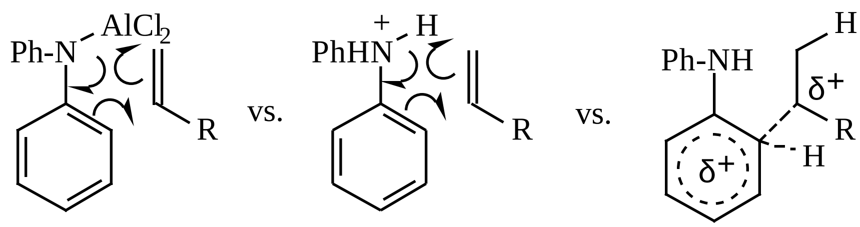
Stereochemical Control vs. Termination (MW)

Lubrizol – Anne Chaka

Study intermediates and components of lubricant additives not otherwise isolable: reduce waste, design continuous process, optimize additive.

- **Test Cheaper/Safer Replacements for $AlCl_3$ & BF_3 in Additive Synthesis**

  Transition State Modeling



  Can't combine catalysts in continuous process!

- **Optimum Polysulfide for Corrosion Inhibition**

  $R\text{-}S\text{-}(S)_n\text{-}R$

  n = 1-5 protects Fe in gears

  n > 2 corrodes Cu alloys

  DFT Fast Structure Code

  Model Stability w/ & w/o Cu Oxide "Catalysis"

$$R-S-(S)_n-R \longrightarrow R\text{-}S\bullet + \bullet(S)_n\text{-}R$$

$$R-S-(S)_n-R + CuOH \longrightarrow R\text{-}S(CuOH) + \bullet(S)_n\text{-}R$$

Ford - Bill Schneider

Design exhaust catalyst for pollution control with lean operation (excess O_2) for increased fuel economy. Manipulate Cu environment in zeolite to avoid NO_x in 3-Way Catalyst. Control BaO surface to store NO_x w/o $BaSO_4$ in Dual Mode Converter.

- **Catalysts Convert CO and NO_x**

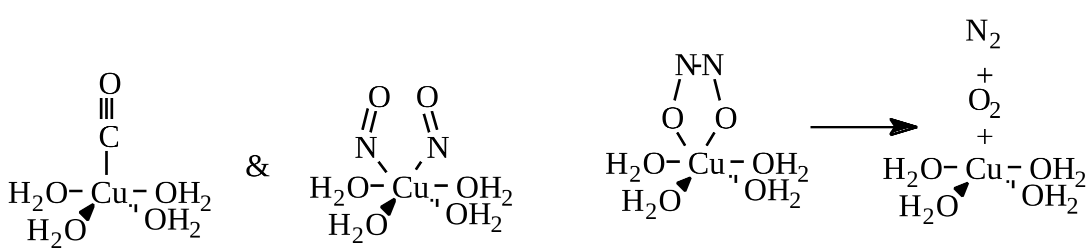
$$NO_x + [H] \longrightarrow NH_3 \quad \text{(HC rich atmosphere)}$$

$$CO + [O] \longrightarrow CO_2$$

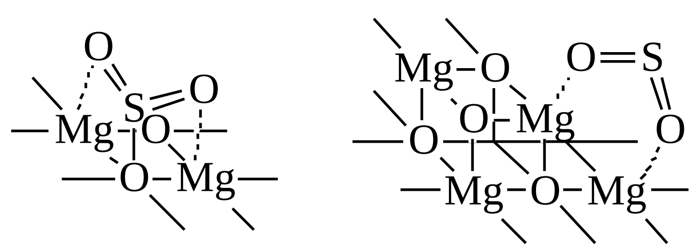
$$NO \longrightarrow N_2 + O_2$$

$$NO + O_2 \not\longrightarrow NO_x \quad \text{(HC lean)}$$

- **Model Binding of CO, NO, H_2O to Supported Cu/ZSM-5 by DFT.**



- **Model binding of NO_x, SO_2 & SO_3 on Ba/MgO [100] surface and step with Car-Parinello DFT/MD.**



Procter & Gamble – Bill Laiding

Understand unique property of component in support of deodorant patent.

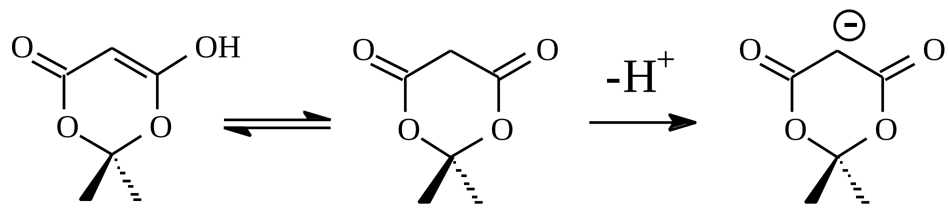
- **Meldrum's Acid Unusually Acidic**

  $pKa_{(DMSO)}$ = 7.3

  Acyclic (Malonate) $pKa_{(DMSO)}$ = 15.9

- **Model Molecules, Tautomers, and Ions to Calculate Acidity**

  MP2/6-311^{++}G** for ions



Enol Disfavored

Different Acidities for Axial & Equatorial H

PPG – Rick Ross

Design inorganic pigments & predict photochromic colors and activity.

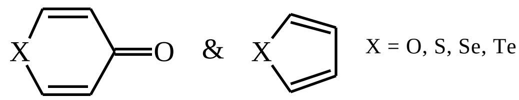
- **Color an Electronic Process**
  - **Promote an Electron into an Unfilled Orbital**
  - **Energy Difference Determines Wavelength Absorbed**
  - **ZINDO CI for Good Unfilled Orbital Energies**

- **Photochromism**
  - **Color vs. MeO- substitution on PNA's**
  - **Promote Electron from Excited State Instead of Ground State**

Eastman Kodak – John McKelvey, Peter Margl

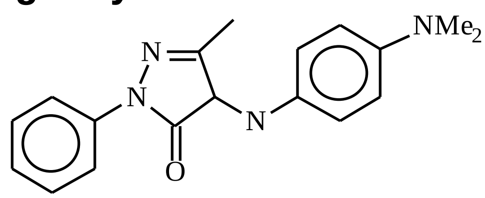
Checking experimental results, predicting electronics and colors for film and photocopier application, alkylation process improvement.

- **Chalcogenic Heterocycles**
  - **Stabilization of Charge Important for Photocopier**
  - **Anomalous Experimental Se Pyran Dipole Moment**



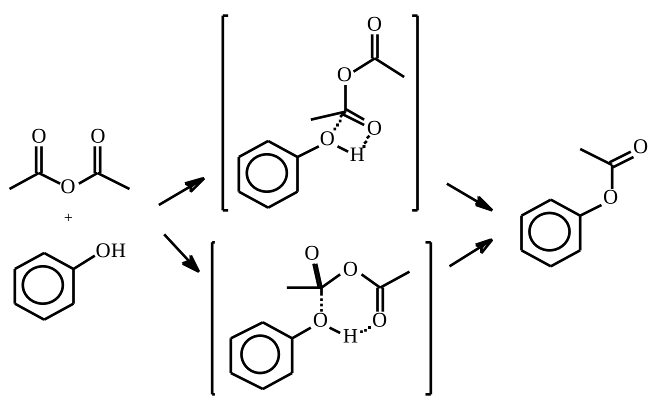
  - **Range of Methods, PM3 Through DFT**
  - **Identified Error in Workup of Lab Data!**

- **Predicting Color of Pyrazalene Dyes**
  - **ZINDO for Large Systems**



  - **Color & Intensity Controlled by Geometry**

- **Accelerate Phenol Acylation Process.**
  - **Acid vs Base Catalysis of Acyl Transfer Reaction**
  - **B3LYP with SCI-PCM for Solvation.**



Acyl Transfer Rate Not Limiting; Solubility Limited!