Organic Chemical Reactions in High-Temperature Water

Phillip E. Savage
University of Michigan
Ann Arbor, MI USA

MichiganEngineering

High-Temperature Water (HTW)

- Water near its critical point (374 °C, 218 atm).
  - Properties between gas and liquid
- Inexpensive and non-toxic.
- Low dielectric constant and fewer hydrogen bonds.
  - High solubility for gases and organics.
  - Single phase at reaction conditions
- High ion product (10^3 times ambient):
  - Acid/base catalysis (H_3O^+, OH^-).
- Tune fluid properties with T and P:
  - Optimization of the reaction environment.
  - Ease of product separation.

MichiganEngineering

Reactions in HTW

(Savage et al., *AIChE J.* 41, 1723, 1995: Savage, *Chem. Rev.*, 99, 603, 1999)

- Alcohol dehydration to olefin
- C-C bond formation.
  - Friedel-Crafts Alkylation
  - Heck arylation
  - Diels-Alder cycloaddition
- Selective partial oxidation
  - Methane, methylaromatics
- Hydrogenation/Dehydrogenation
- Elimination
  - CO_2 from acids, halogens

MichiganEngineering

Organic Chemical Reactions in HTW

core competencies

- Experiments
  - Flow and batch reactors
  - Catalytic and noncatalytic reactions
- Kinetics, Mechanisms, and Modeling
  - Phenomenological models (engineering kinetics)
  - Mechanistic models (detailed chemical kinetics)
- Computation and Simulation
  - Computational quantum chemistry
  - Molecular dynamics simulation

MichiganEngineering

Chemical Synthesis at Supercritical Conditions

- Current commercial chemical processes
  - Ethylene polymerization
  - Ammonia synthesis
  - Methanol synthesis

Roles for Water: Rxns in HTW

- Potential acid catalyst
  - Water has a natural supply of H^+
  - $[H^+]$ strong function of temperature and density
  - Cyclohexanol dehydration
- Interact with reactants (hydrogen bonding)
  - Formic acid decomposition
- Differential solvation along reaction coordinate
  - Preferential solvation for transition state or reactants will affect kinetics
  - H_2O_2 dissociation

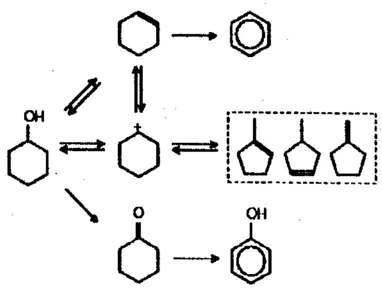
Cyclohexanol Chemistry in HTW

Model reaction system.

Reactions: Dehydration, rearrangement, dehydrogenation, aromatization, and rearrangement.

Goal: Determine the influence of T, P, ρ, pH, and catalysts on rates of different paths in HTW.

Outcome: Use knowledge gained to control chemical reactions in HTW.



Cyclohexanol Dehydration in HTW

- Acid-catalyzed reaction - Will it occur in HTW in the absence of added acid?
- Very limited previous work:
  - Crittendon & Parsons (1994) – No reaction at 375 °C and 20 minutes in pure HTW.
  - Kuhlmann et al. (1994) – 33% conversion at 300 °C and 60 minutes in pure HTW, cyclohexene the only product.
  - No kinetics or mechanisms available.
- **Existing data are few & apparently contradictory!**

Experimental Procedure

- Reaction conditions:
  - $[\text{cyclohexanol}]_0$ = 0.3 mol/L
  - T = 250-380 °C
  - ρ_{H_2O} = 0.08-0.81g/cc
  - t = 15-180 min.
- Stainless steel batch microreactors (V = 0.59 mL), 2-3 min heat-up time.
- Condition reactors hydrothermally prior to use.
- Single phase (liquid or supercritical) at all reaction conditions by adjusting the water loading. Organic compounds are water-soluble at reaction conditions.

MichiganEngineering

Experimental Procedure

- Distilled, de-ionized water, sparged by helium immediately before use.
- Load and seal reactors in helium-filled glove bag.
- Immerse reactors in pre-heated, isothermal, fluidized sandbath.
- Remove from sandbath, quench in cold water (room temperature after ~1 min.).
- Cool in freezer to condense volatile products.

MichiganEngineering

Experimental Procedure

- Recover reactor contents by addition of acetone.
- Product analysis by GC-FID and GC-MS.
  - HP-5 capillary column for separation of components.
  - Standard – methyl cyclohexane.
- Multiple experiments at each condition to get experimental uncertainties.

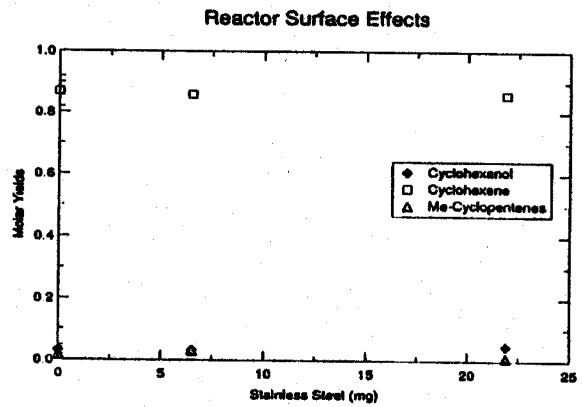
MichiganEngineering

Effects of Dissolved Gases

- Dissolved air – CO_2 (carbonic acid), O_2 (oxidant).
- Use un-degassed water in experiments to see effects.
- No difference in cyclohexanone yields – impact of dissolved O_2 is negligible.
- Increase in rate of cyclohexanol dehydration and methyl cyclopentenes formation.
- Effects greatest at low densities and short times.
- For rigorous kinetics studies, it is important to remove these gases from water prior to use.

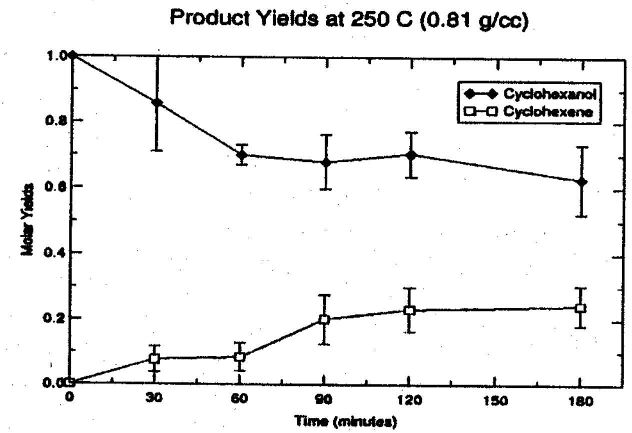
MichiganEngineering

Effect of Metal Surface



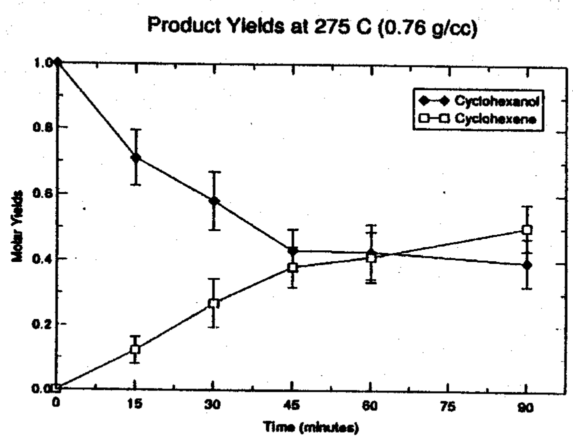
Michigan**Engineering**

Experimental Results - 250°C



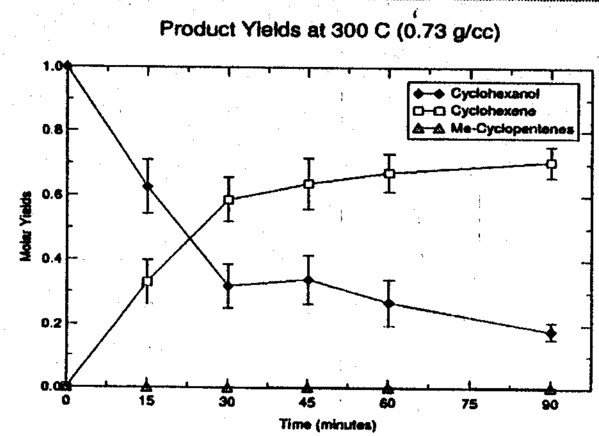
Michigan**Engineering**

Experimental Results - 275°C



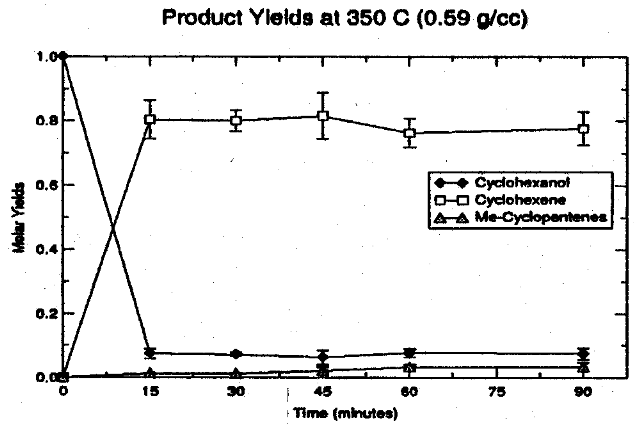
Michigan**Engineering**

Experimental Results - 300°C



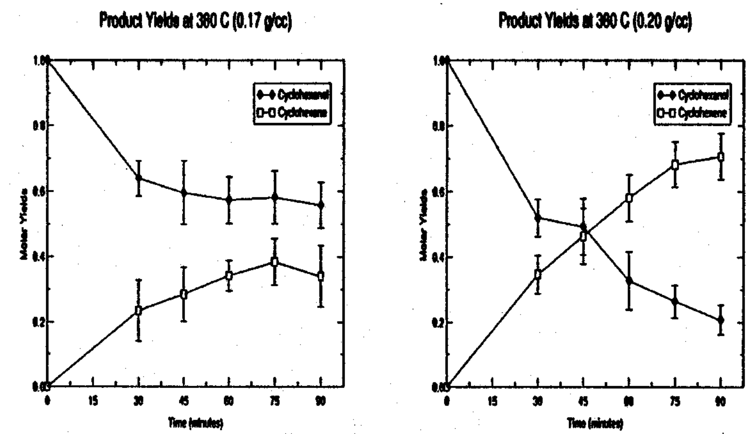
Michigan**Engineering**

Experimental Results - 350°C



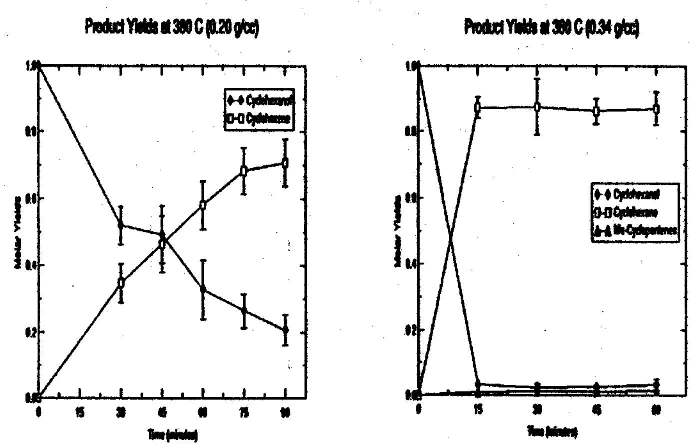
MichiganEngineering

Experimental Results - 380°C



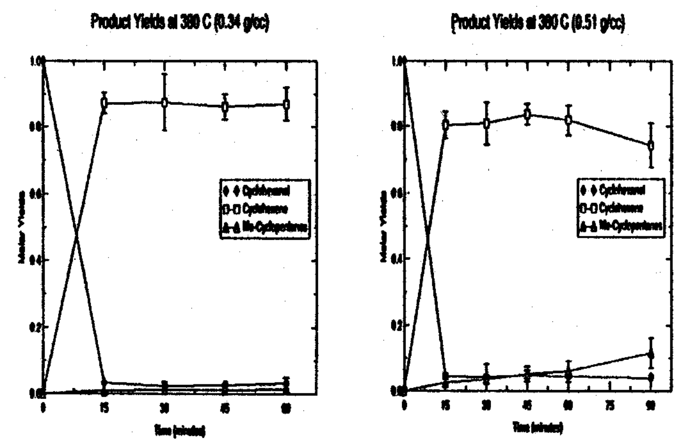
MichiganEngineering

Experimental Results - 380°C



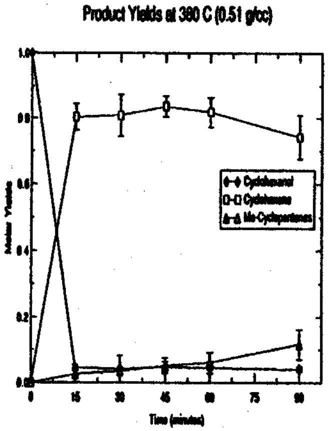
MichiganEngineering

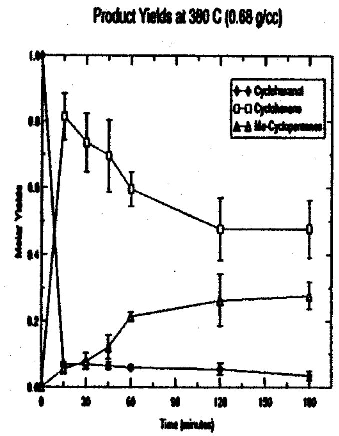
Experimental Results - 380°C



MichiganEngineering

Experimental Results - 380°C





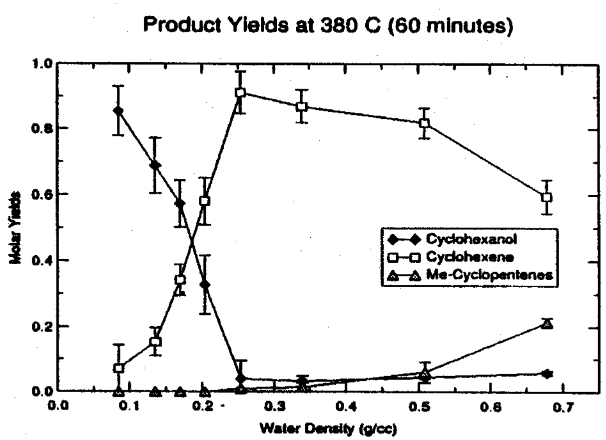
MichiganEngineering

Comparison with Past Studies

This Work	Previous Work	Explanation
> 90% conversion at 380 °C, 15 min.	Crittendon & Parson: No reaction at 375 °C, 20 min.	Very slow reactor heat-up (only 268 °C after 20 min in 375 °C furnace). Vapor and liquid phases present in the reactor.
> 60% cyclohexene yield at 300 °C, 60 min.	Kuhlmann et al.: 33% cyclohexene yield at 300 °C, 60 min.	Possible loss of some volatile products when opening reactors due to insufficient cooling before sampling.

MichiganEngineering

Effect of Water Density at 380°C



MichiganEngineering

Summary of Experimental Data

- Cyclohexanol dehydration occurs readily in HTW.
- Major product is cyclohexene, by-products are 1- and 3-methyl cyclopentenes.
- When the methyl cyclopentenes yield increases, the cyclohexene yield decreases, but the cyclohexanol conversion is unchanged.
- Rate of cyclohexanol disappearance and selectivity toward methyl cyclopentenes increase with increasing temperature and water density.
- Reaction rate is very low at very low water densities (below ~0.1 g/cc).

MichiganEngineering