

Organic Chemical Reactions in High-Temperature Water

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



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
 - CO₂ from acids, halogens



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 (10³ times ambient):
 - Acid/base catalysis (H₃O⁺, OH⁻).
- Tune fluid properties with T and P:
 - Optimization of the reaction environment.
 - Ease of product separation.



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



Chemical Synthesis at Supercritical Conditions

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



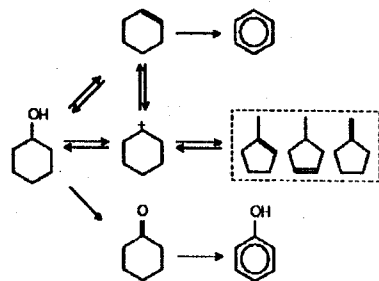
Cyclohexanol Chemistry in HTW

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.



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 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:
 - $[\text{cyclohexanol}]_0 = 0.3 \text{ mol/L}$
 - $T = 250\text{-}380 \text{ }^\circ\text{C}$
 - $\rho_{\text{H}_2\text{O}} = 0.08\text{-}0.81 \text{ g/cc}$
 - $t = 15\text{-}180 \text{ min.}$
- Stainless steel batch microreactors ($V = 0.59 \text{ mL}$), 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.



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.



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.

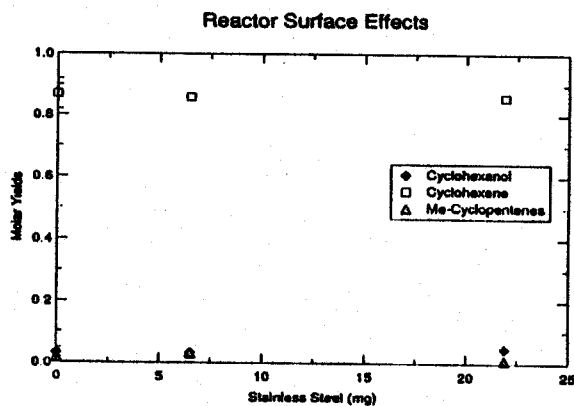


Effects of Dissolved Gases

- 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 cyclopentenones 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.

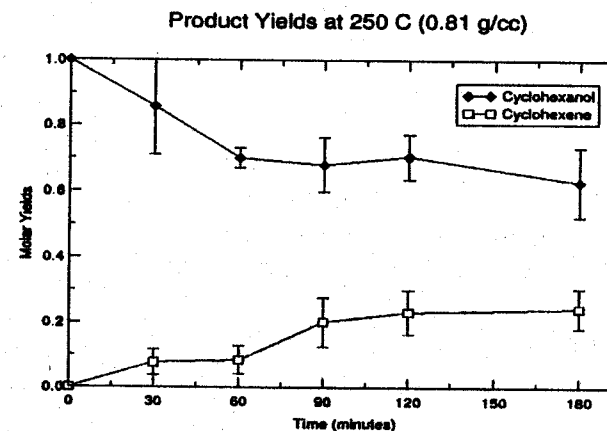


Effect of Metal Surface



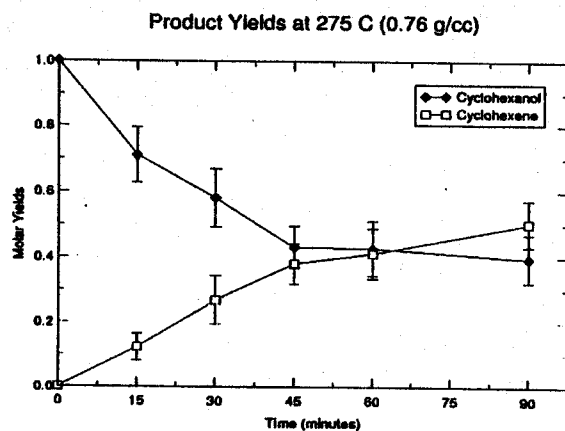
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Experimental Results - 250°C



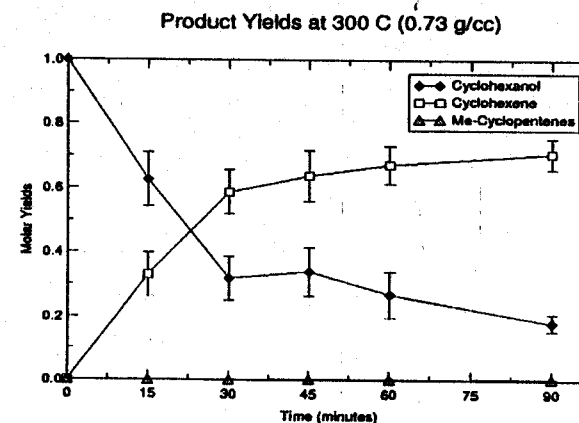
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Experimental Results - 275°C



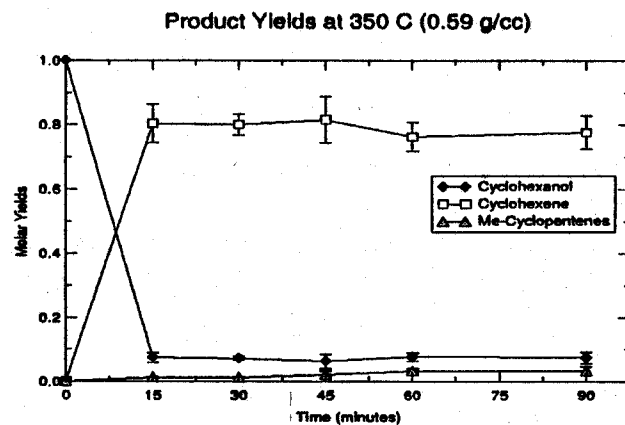
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Experimental Results - 300°C

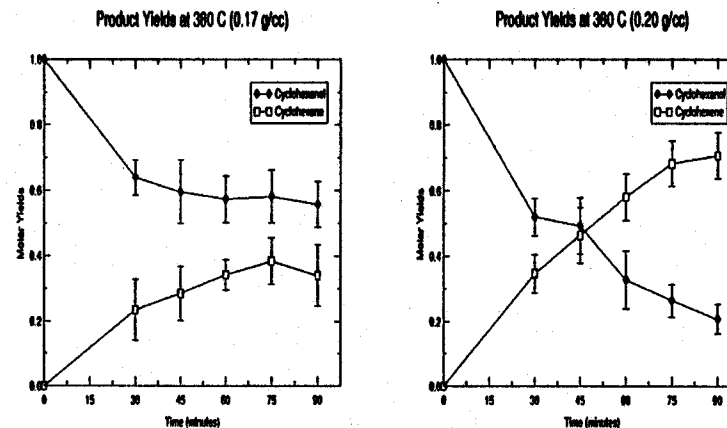


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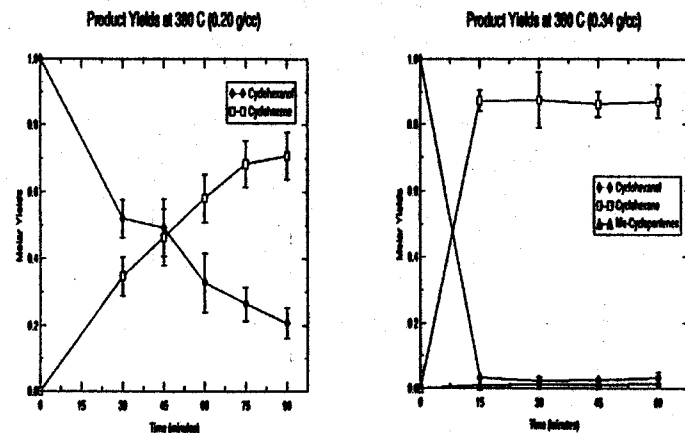
Experimental Results - 350°C



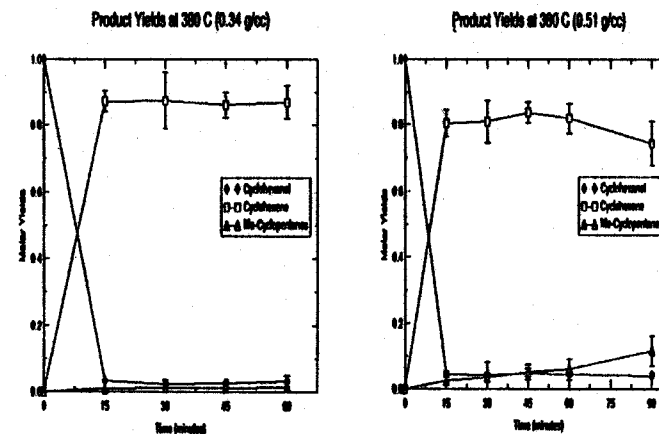
Experimental Results - 380°C



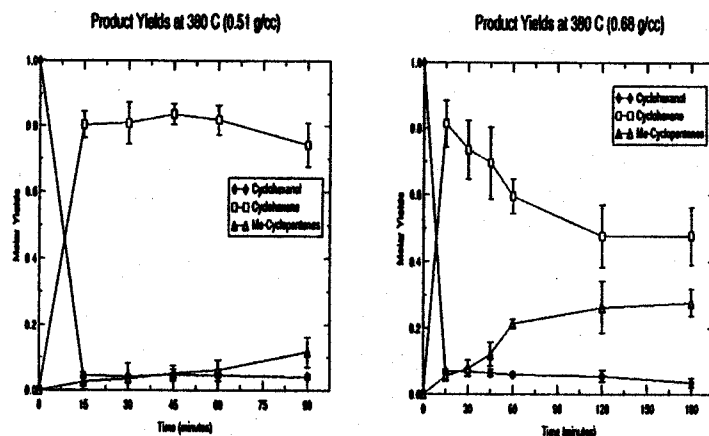
Experimental Results - 380°C



Experimental Results - 380°C



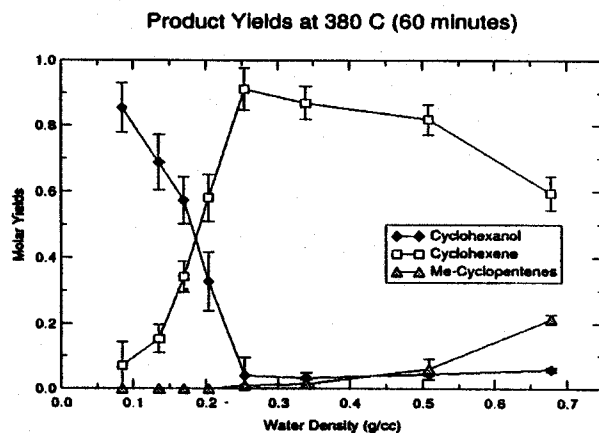
Experimental Results - 380°C



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.

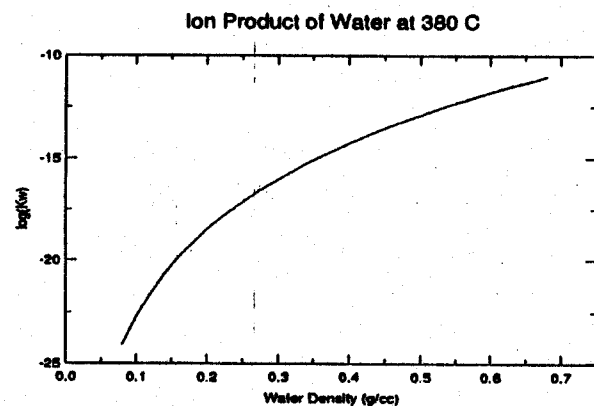
Effect of Water Density at 380°C



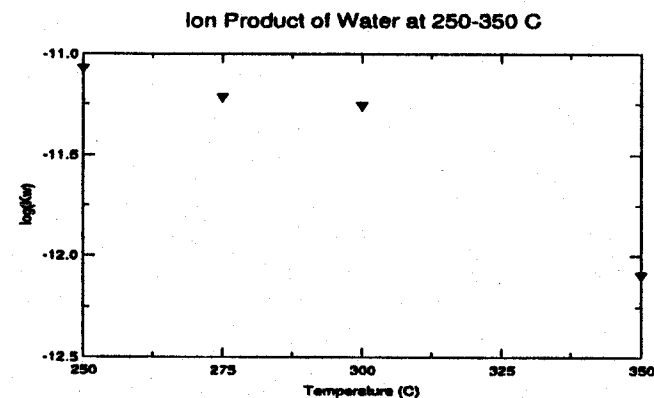
Summary of Experimental Data

- 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).

Effect of Water Density on K_w at 380°C



K_w at Experimental Conditions



Reaction of Cyclohexene in HTW

- Cyclohexene as the starting material (t = 60 min).

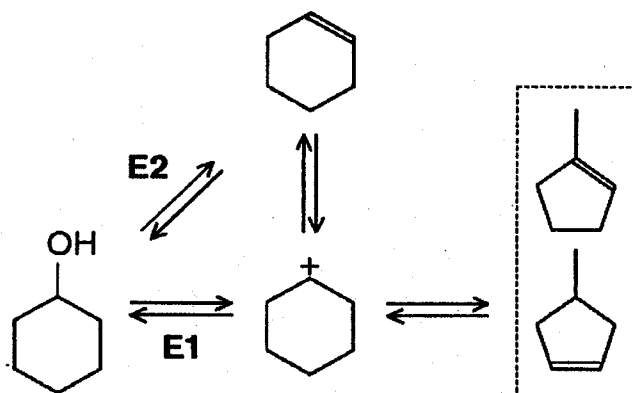
T (°C)	Cyclohexanol Yield	Me-Cyclopentenenes Yield
300	14.3 ± 6.1%	1.7 ± 1.6%
380	2.7 ± 0.5%	15.3 ± 6.0%

- 2 paths: (1) hydration of cyclohexene and (2) rearrangement.
- Different paths preferred at different temperatures.

Alcohol Dehydration Mechanisms

- Classic organic chemistry – E1cB, E1, and E2.
 - E1cB – occurs in the presence of strong base, via carbanion intermediate.
 - E1 – occurs in the presence of strong acid, via carbocation intermediate.
 - E2 – occurs in the presence balanced acidity/basicity; concerted elimination of H and OH.
- Dominant mechanism not always clear, depends on catalyst, reaction medium, temperature, and alcohol structure.
- Our candidate mechanisms – E1 or E2.

E1 vs. E2 Mechanisms



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Carbocations in Water

- Gas-phase deuterium-labeling experiments gave evidence for carbocations as the intermediates in cyclohexanol dehydration → E1 mechanism?
- Solvation may play an important role in HTW!
 - Direct spectroscopic observation of carbocations only in anhydrous superacids, not in dilute (aqueous) acid solutions.
 - In water: $R^+ + nH_2O = ROH_2^+(n-1)H_2O \rightarrow E2$.
 - ^{13}C NMR – *t*-butanol dehydrates via ROH_2^+ , not R^+ , even in moderately concentrated (>70%) H_2SO_4 .
- Oxonium ions appear to be more stable in water.

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Carbocations in HTW

- Are carbocations any more or less stable in HTW?
- Shift in mechanism with reaction condition is possible.
- Changes in product distribution suggests that dehydration mechanism changes from E2-like to E1-like as the temperature increases.
 - 1,2-diphenyl-2-propanol over alumina.
 - *t*-pentanol over TiO_2 .
 - 2-butanol on ThO_2 .
- Even in water, formation of carbocations may become more favorable at higher temperatures.

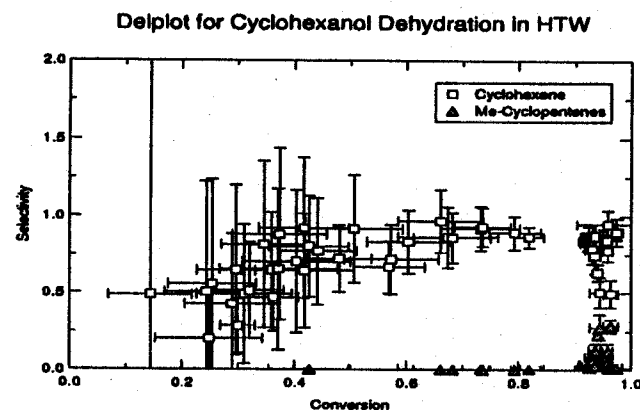
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Cyclohexanol Dehydration in HTW

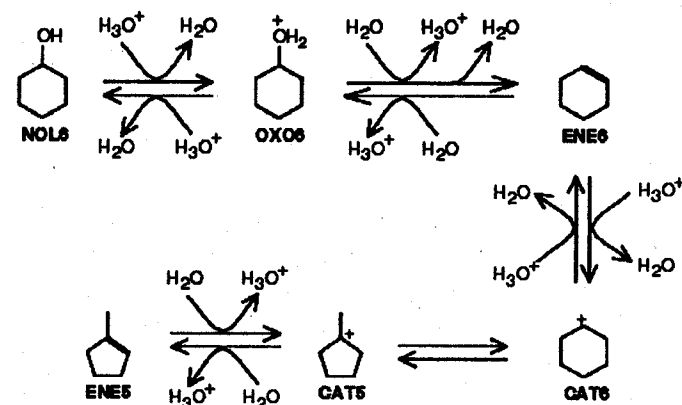
- If E1 mechanism is dominant, major product should be 1-methyl cyclopentenés (most stable, from carbocation rearrangement).
- We observe cyclohexene as the major product → E2 mechanism should be dominant.
- Methyl cyclopentenés observed at $T > 300^\circ C \rightarrow$ carbocation formation becomes more favorable at high temperatures.
- $380^\circ C$ data suggest increasing water density also favors carbocation formation.
- Source of carbocation – (1) cyclohexanol (E1) or (2) cyclohexene (E2).

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Product Selectivities



Proposed Reaction Mechanism



Detailed Kinetics Model

$$\frac{d[\text{NOL6}]}{dt} = -k_{01}[\text{H}_3\text{O}^+][\text{NOL6}] + k_{10}[\text{H}_2\text{O}][\text{OXO6}]$$

$$\frac{d[\text{OXO6}]}{dt} = k_{01}[\text{H}_3\text{O}^+][\text{NOL6}] - (k_{10} + k_{12})[\text{H}_2\text{O}][\text{OXO6}] + k_{21}[\text{H}_2\text{O}][\text{H}_3\text{O}^+][\text{ENE6}]$$

$$\frac{d[\text{ENE6}]}{dt} = k_{12}[\text{H}_2\text{O}][\text{OXO6}] - (k_{21}[\text{H}_2\text{O}] + k_{23}[\text{H}_3\text{O}^+])[\text{ENE6}] + k_{32}[\text{H}_2\text{O}][\text{CAT6}]$$

$$\frac{d[\text{CAT6}]}{dt} = k_{23}[\text{H}_3\text{O}^+][\text{ENE6}] - (k_{32}[\text{H}_2\text{O}] + k_{34})[\text{CAT6}] + k_{43}[\text{CAT5}]$$

$$\frac{d[\text{CAT5}]}{dt} = k_{34}[\text{CAT6}] - (k_{43} + k_{45}[\text{H}_2\text{O}])[\text{CAT5}] + k_{54}[\text{H}_3\text{O}^+][\text{ENE5}]$$

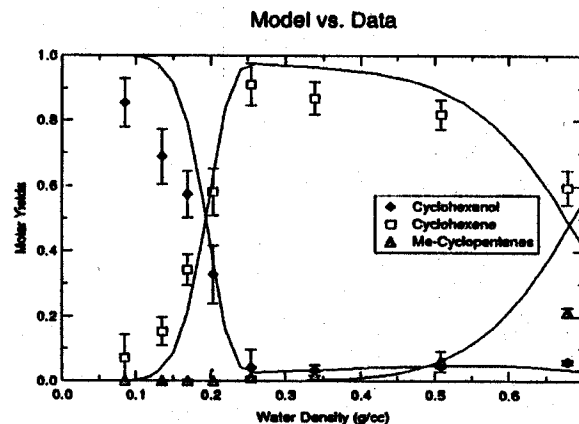
$$\frac{d[\text{ENE5}]}{dt} = k_{45}[\text{H}_2\text{O}][\text{CAT5}] - k_{54}[\text{H}_3\text{O}^+][\text{ENE5}]$$

Parameter Estimation

- Fit the experimental concentration profiles to the model by adjusting the rate constants.
- Simultaneous numerical solution of ODEs and parameter estimation, using Scientist®.
- Iterative procedure:
 - Separate fitting for each value of water density.
 - Calculate average parameters.
- Goal – determine whether the model (i.e. mechanism) properly accounts for the role of water (catalyst, reactant, product).

Model and Experimental Results

380°C, 60 minutes



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Summary

- Cyclohexanol dehydrates readily in pure HTW, forming cyclohexene and methyl cyclopentenes.
- Increases in temperature and water density enhance rate of cyclohexanol disappearance and methyl cyclopentenes formation.
- High reactivity of cyclohexanol relative to literature data is due to improved experimental procedures.
- Cyclohexanol dehydration proceeds via E2 mechanism, but carbocation formation becomes more favorable with increasing temperature and water density.
- Water is not an inert solvent but is an integral component of the reaction.

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Roles for Water in Cyclohexanol Dehydration

- Water is an integral part of the reaction:
 - Water participates as a reactant and product.
 - Water is the source of H_3O^+ , the acid catalyst.
 - Water drives the reaction mechanism toward E2 by solvation, favoring the oxonium ion rather than the carbocation as the reaction intermediate.
- We can expect similar contributions in the dehydration of other alcohols in HTW, depending on the alcohol structure and reaction conditions.

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Experimental Observations for Formic Acid Decomposition

Gas Phase
(Blake et al., 1971)

$\text{CO}/\text{CO}_2 \approx 10/1$

$k(700\text{K}) \approx 10^{-7} \text{ 1/s}$

Aqueous Phase
(Yu & Savage, 1997)

$\text{CO}/\text{CO}_2 \approx 1/100$

$k(700\text{K}) \approx 10^{-1} \text{ 1/s}$

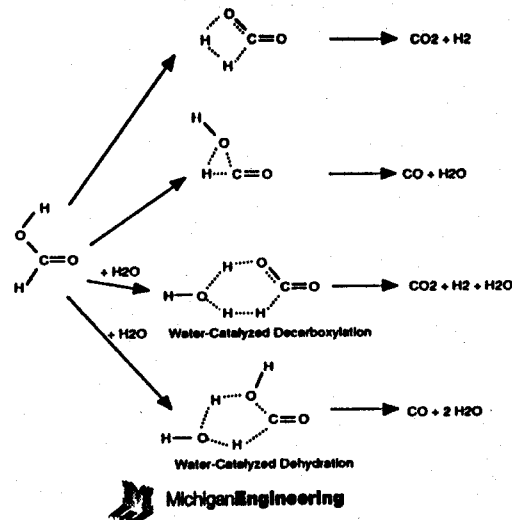
Decomposition is much faster in aqueous phase

CO is main product in gas phase, CO_2 in aqueous phase

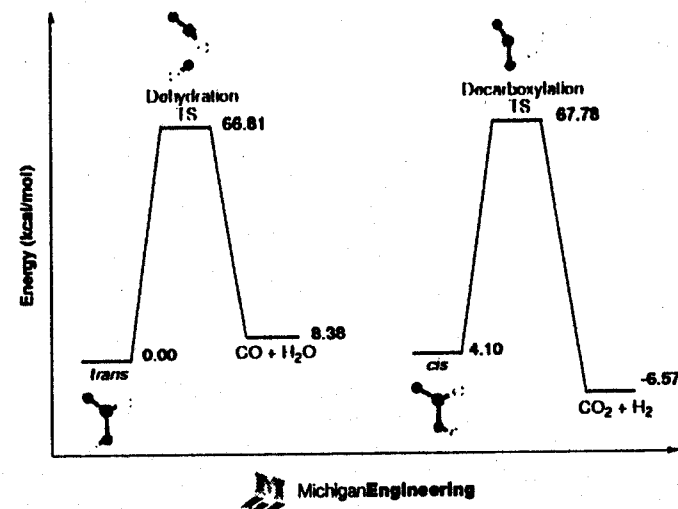
How is water influencing the rate and selectivity?

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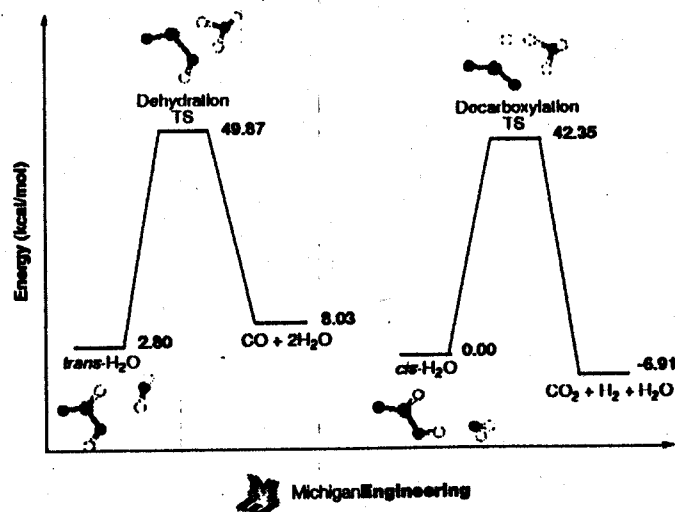
Molecular Mechanisms for Formic Acid Decomposition



Energy Diagram for Formic Acid Decomposition (gas phase)



Energy Diagram for Formic Acid Decomposition (with water)



Exptl. & Quantum Chem. Results for Formic Acid Decomposition

(Akiya & Savage, *AIChE J.*, 44, 405, 1998)

	Gas Phase		Aqueous Phase	
	Exptl.	Calc.	Exptl.	Calc.
CO ₂ /CO	10 ⁻¹	10 ⁻¹	10 ²	10 ²
k@700K	10 ⁻⁷	10 ⁻⁷	10 ⁻¹	10 ^{-3-10⁰}

- Water molecules interact with and stabilize transition states
- These interactions influence both kinetics and selectivity

H₂O₂ Dissociation in Supercritical Water

- Extremely important reaction in SCWO
 - $\text{H}_2\text{O}_2 = 2 \text{ OH}$
- Experimental observations (*AIChE J.*, 43, 2343, 1997)
 - Rate faster in SCW than in gas phase at same pressure
 - Rate at 34.0 MPa lower than rate at 24.5 MPa



Molecular Dynamics Simulations

(Akiya and Savage, *J. Phys. Chem. A* 104, 4433 & 4441, 2000)

- Do MD simulations to calculate ΔA_{solv} and Δv^\ddagger
- Need intermolecular potential function (partial charges, LJ parameters) to do MD simulations
- Used DFT calculations to get force field parameters for H₂O₂-water interactions
- 499 water molecules and 1 H₂O₂
- $T_r=1.15$, $\rho_r=1.25$ for ΔA_{solv} calculations
- $T_r=1.15$, $\rho_r=0.25\text{-}2.75$ for Δv^\ddagger calculations



H₂O₂ Dissociation in SCW

(Akiya and Savage, *J. Phys. Chem. A* 104, 4433 & 4441, 2000)

Gas-phase and SCW-phase rate constants related by change in free energy of solvation (ΔA_{solv})

$$k_{\text{SCW}} = k_G \exp(-\Delta A_{\text{solv}}(r^\ddagger)/RT)$$

Effect of density on rate constant related to activation volume (Δv^\ddagger)

$$(\partial \ln k / \partial \rho)_T = (-\Delta v^\ddagger / \rho RT \kappa_T)$$

$$\Delta v^\ddagger = \bar{v}_{\text{TS}} - \bar{v}_{\text{H}_2\text{O}_2}$$

Use MD simulations to calculate ΔA_{solv} and Δv^\ddagger



Free Energy of Solvation for H₂O₂ Dissociation in SCW

(Akiya and Savage, *J. Phys. Chem. A* 104, 4433 & 4441, 2000)

From MD simulations

$$k_{\text{SCW}} = k_G \exp(-\Delta A_{\text{solv}}(r^\ddagger)/RT) = (2.09/RT) = 1.44$$

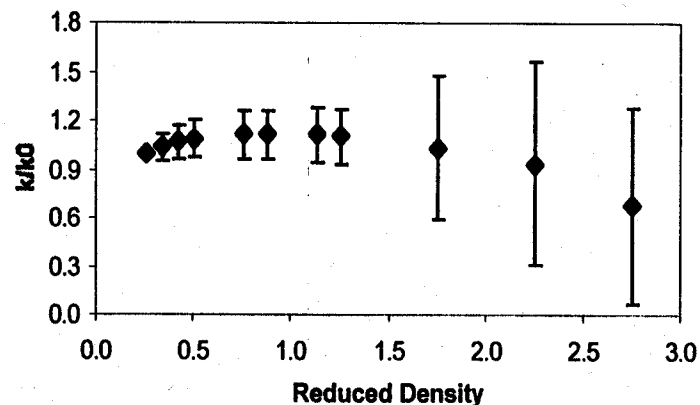
From literature data

$$(k_{\text{SCW}}/k_G) = 3.27$$

$$\text{with uncertainty } 1.01 < (k_{\text{SCW}}/k_G) < 10.6$$



Effect of SCW Density on Rate Constant for H_2O_2 Dissociation



Summary and Conclusions

- Reaction rates in HTW can be density dependent.
- HTW contains a native H^+ conc. sufficient for acid-catalyzed reactions. The H^+ conc. and rate and selectivity can be controlled by controlling the water density
- Water molecules can interact with reactants and transition states to alter kinetics and selectivities.
- Density-induced changes in differential solvation along the reaction coordinate can influence HTW reaction rates.



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