

Rate-enhancing roles of water molecules in methyltrioxorhenium-catalyzed olefin epoxidation by H_2O_2

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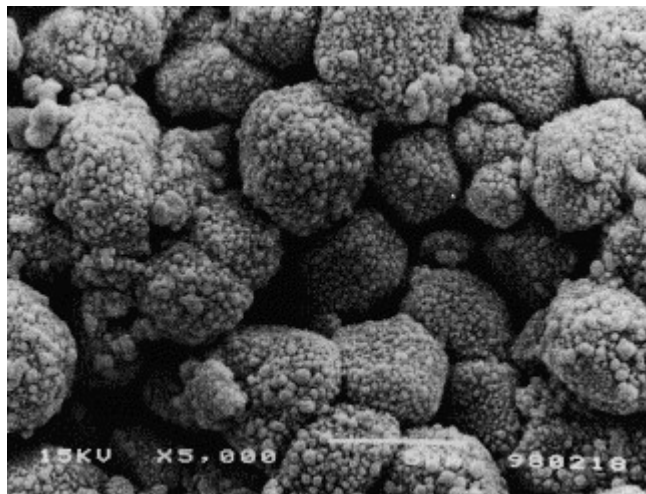
“Greening” the Ethylene Oxide Process

replace $\text{C}_2\text{H}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{C}_2\text{H}_4\text{O} \text{ (+ 2 CO}_2\text{, 15 \%)}$

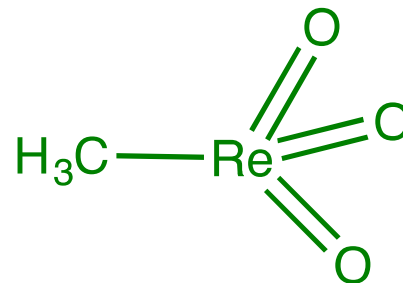
by $\text{C}_2\text{H}_4 + \text{H}_2\text{O}_2 \rightarrow \text{C}_2\text{H}_4\text{O} + \text{H}_2\text{O}$

CH_3ReO_3 (methyltrioxorhenium, MTO)

$\text{CsRe-12 wt.\% Ag}/\alpha\text{-Al}_2\text{O}_3$



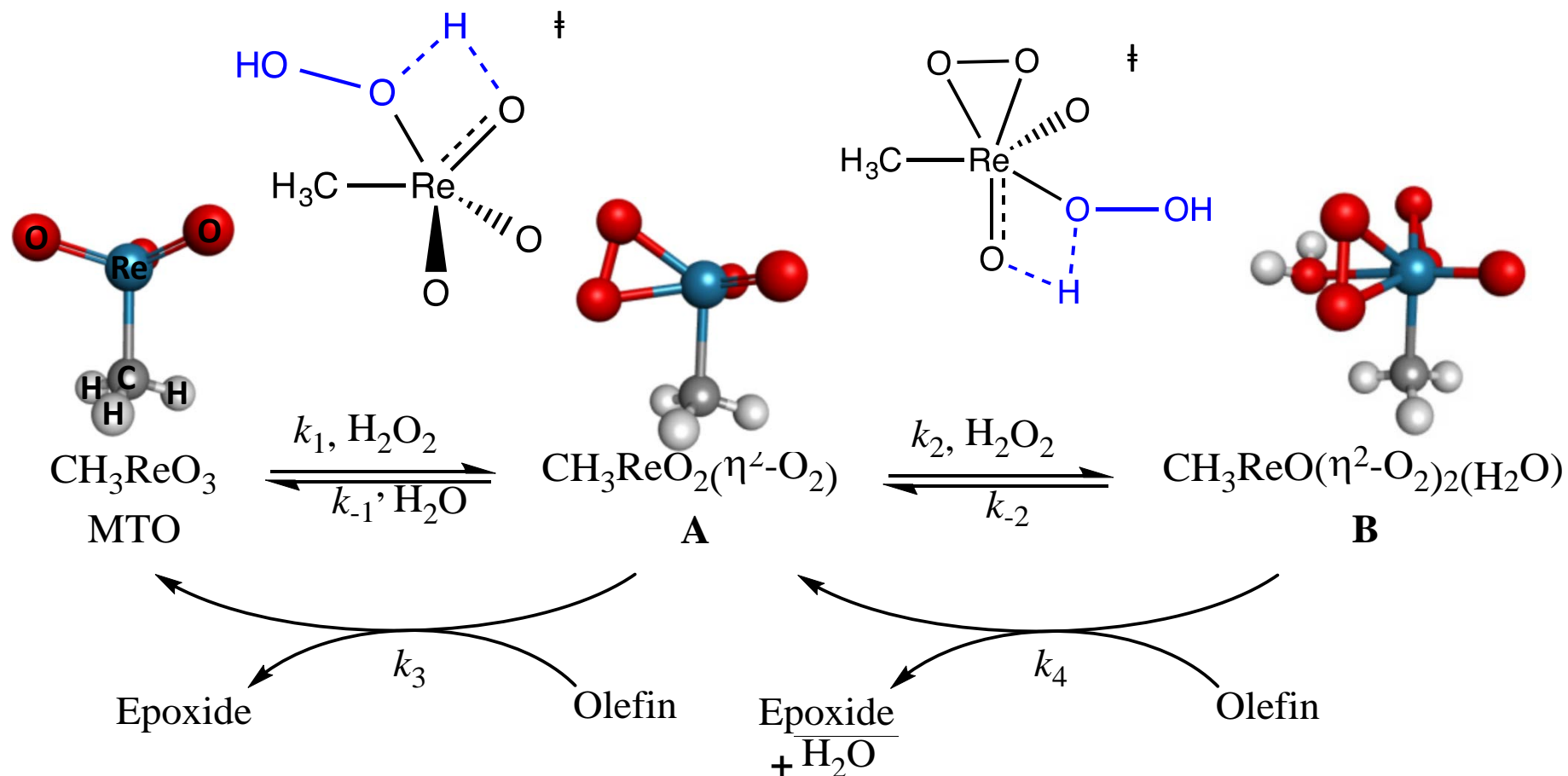
heterogeneous catalyst
10 – 30 bar, 200 – 260 °C



homogeneous catalyst

$\text{C}_2\text{H}_4\text{O}$ selectivity $\approx 100\%$
No H_2O_2 decomposition
Works with higher olefins (e.g., C_3H_6)
20 – 40 °C, 50 – 60 bar

Methyltrioxorhenium activates H_2O_2 for oxygen atom transfer

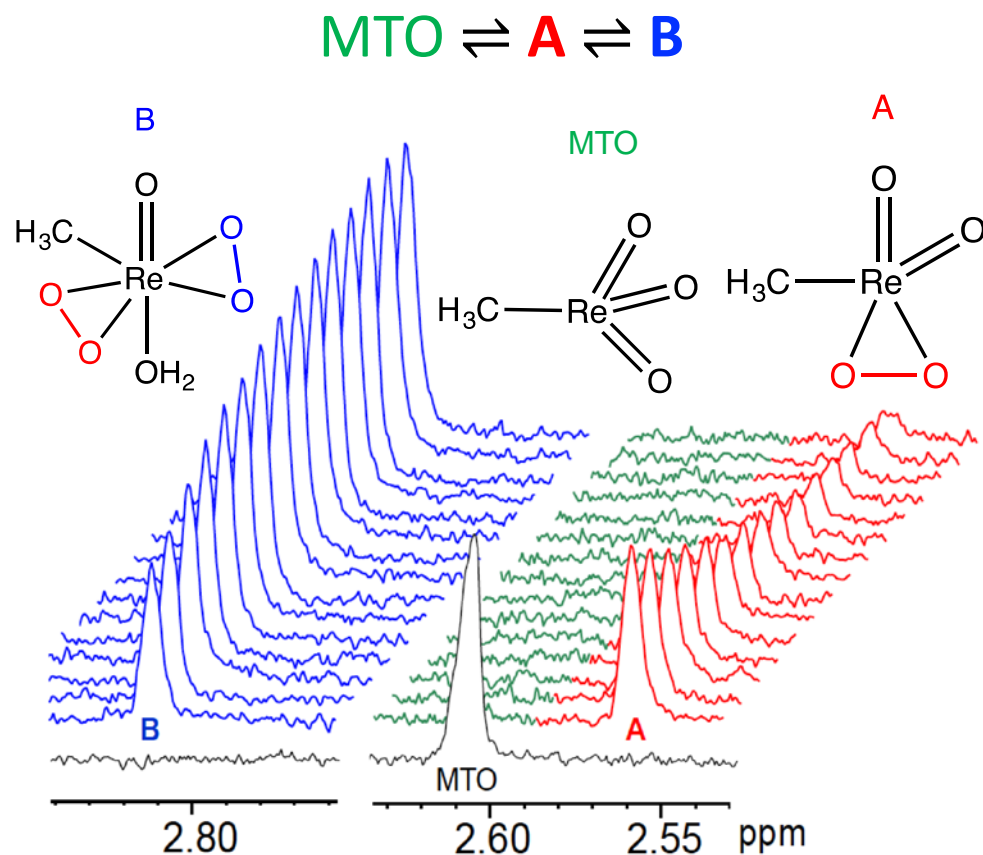


J. H. Espenson, *Chem. Comm.* 479 (1999)

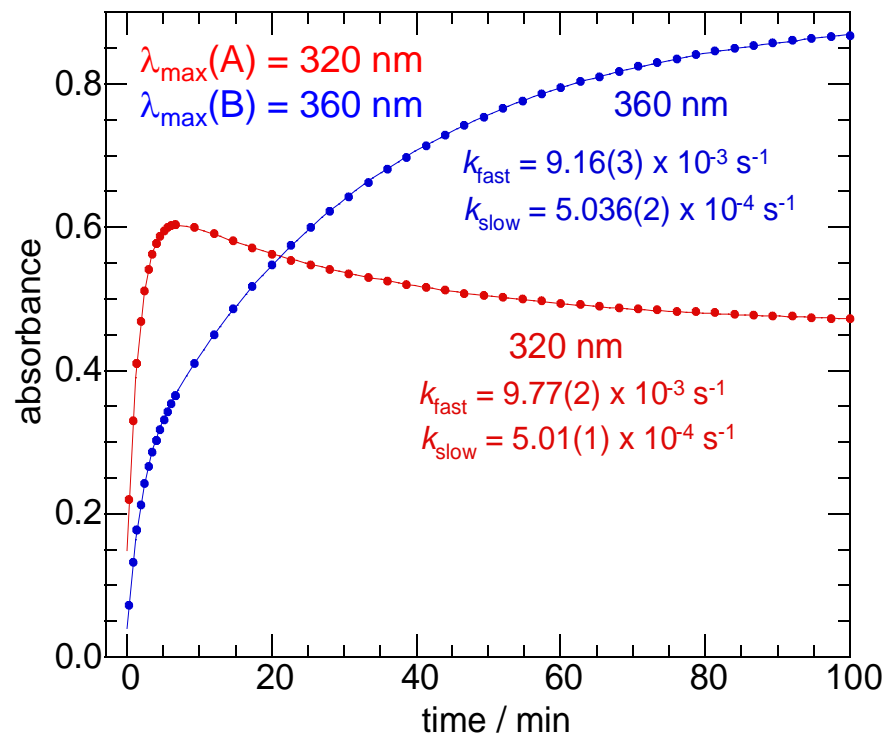
W. A. Herrmann, R. W. Fischer, J. D. G. Correia, *J. Mol. Catal.* 94 (1994)

The 'clean' spectra of MTO make it amenable to kinetic studies

^1H NMR spectra recorded
at 3 minute intervals, 23.0 °C



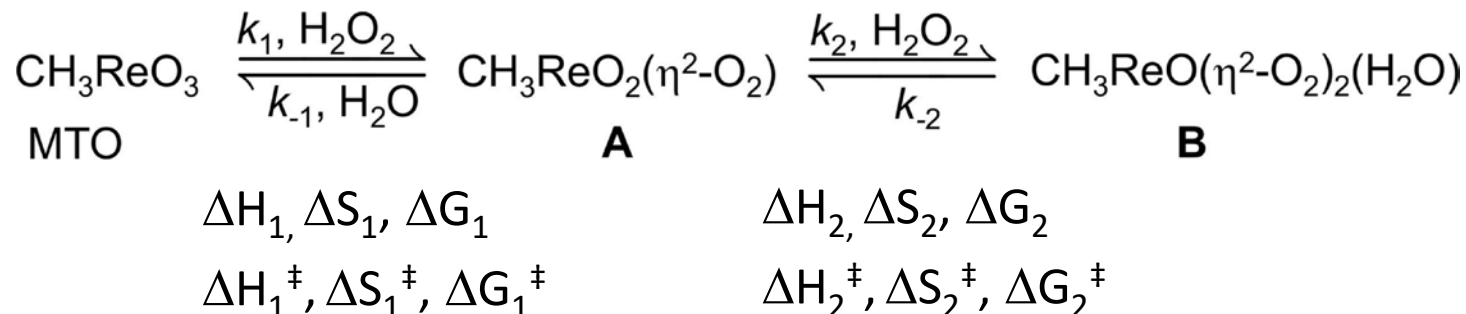
UV-vis spectra recorded
at 1 minute intervals, 25.0 °C



$$A_t = A_\infty + \alpha e^{-k_{\text{fast}} t} + \beta e^{-k_{\text{slow}} t}$$

$$A_t = A_\infty + \alpha(1 - e^{-k_{\text{fast}} t}) + \beta e^{-k_{\text{slow}} t}$$

Although MTO is a highly studied system,
many discrepancies remain between experiment and theory



Thermodynamics

Calculated *Experimental*

$$\Delta H_1 > 0$$

$$\Delta H_1 < 0$$

$$\Delta S_1 < 0$$

$$\Delta S_1 > 0$$

$$\Delta G_1 > 0$$

$$\Delta G_1 < 0$$

$$\Delta G_1 > \Delta G_2$$

$$\Delta G_1 < \Delta G_2$$

$$\text{calc. } \Delta H_2 = \text{exp. } \Delta G_2$$

JACS*, **2015, 137, 9604

Inorg. Chem.*, **2013, 52, 13904

Chem. Eur. J. **2009**, 15, 1862 (in aq. CH₃CN)

Inorg. Chem. **2008**, 48, 307 (in H₂O)

JACS, **2007**, 129, 15794 (in aq. THF)

JACS, **2001**, 123, 2365 (in gas phase)

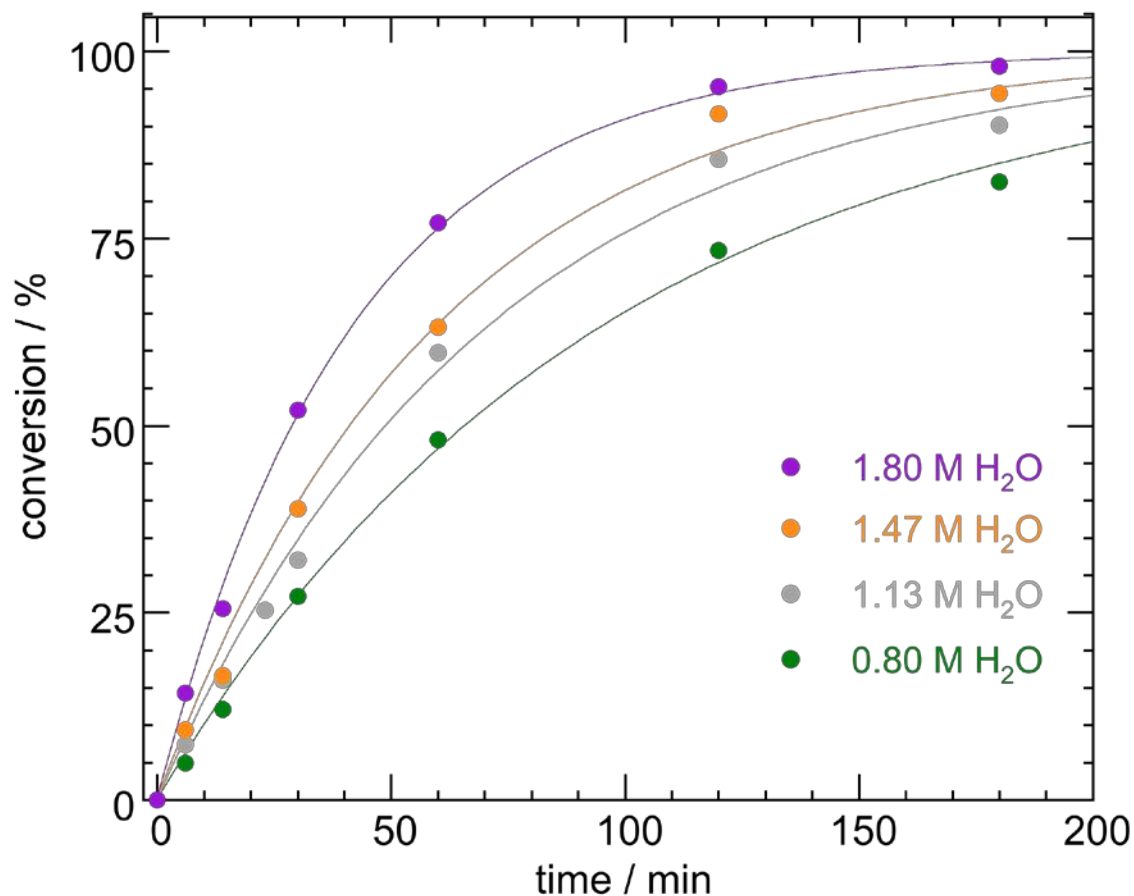
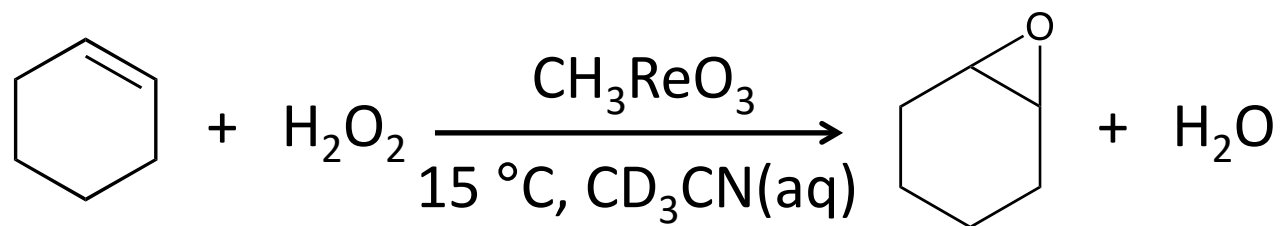
Angew. Chem. Int. Ed. **1998**, 37, 2211 (gas phase)

claimed “excellent agreement”

Kinetics

$$\Delta H_1^\ddagger > 100 \text{ kJ mol}^{-1} \quad (\text{exp. } 24.5 \text{ kJ mol}^{-1})$$

Besides the thermodynamic and kinetic discrepancies, the remarkable water-dependence has yet to be explained



**Strong solvent effect
on the *observed* rate**

$$X = 1 - \exp(-k_{\text{obs}} t)$$

$$k_{\text{obs}} = -k[\text{H}_2\text{O}]$$

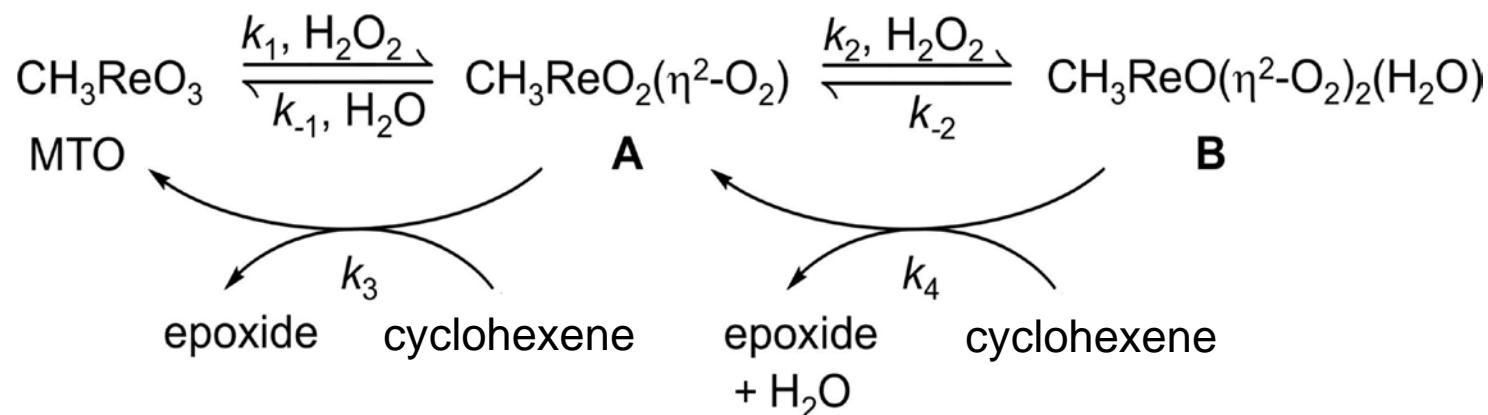
Benchmark the thermodynamics and kinetics of MTO-catalyzed cyclohexene epoxidation: The key role of H₂O

Density-functional theory

Microkinetic modeling

Experimental kinetic measurements

UV-vis, ¹H NMR, proton inventory



In acetonitrile solvent
with 1–4 M [H₂O]

B. R. Goldsmith, T. Hwang, S. Seritan, B. Peters, S. L. Scott, *J. Am. Chem. Soc.* 137 (2015)

T. Hwang, B. R. Goldsmith, B. Peters, S. L. Scott, *Inorg. Chem.* 52 (2013)

First-principles computational approach

Range separated exchange-correlation functional ω B97X-D

J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.* 10 (2008)

Def2-TZVP basis set, with 2 optimized f -orbitals for Re

D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta*, 77 (1990)

Include implicit acetonitrile solvation effects

Geometries optimized in a polarizable continuum model (CPCM)

Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.* 105 (2005)

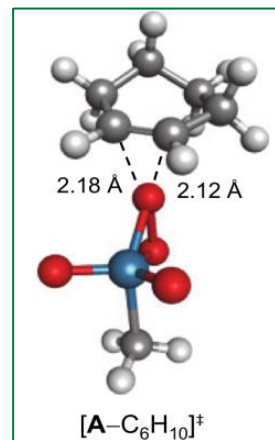
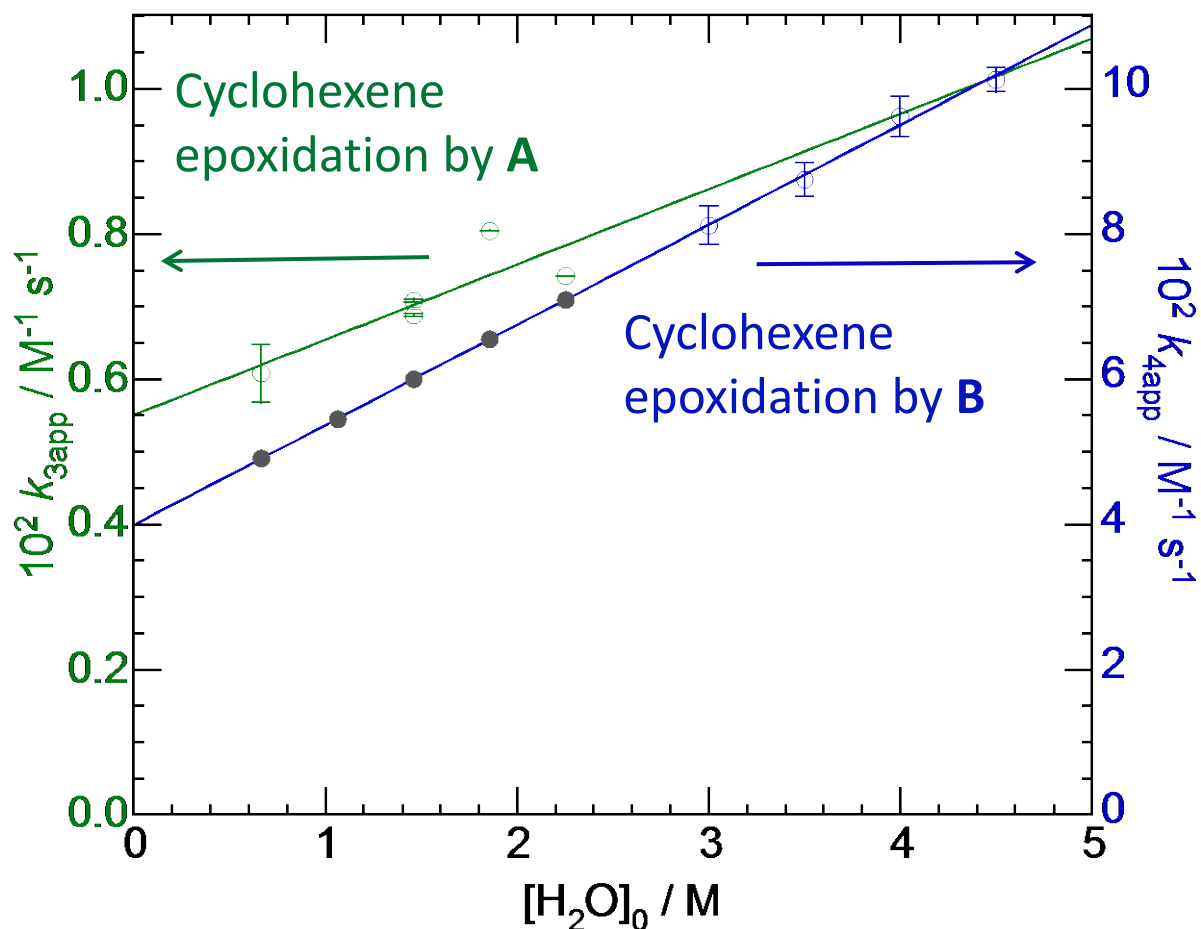
Ideal gas-phase entropies corrected for solvation

D. H. Wertz *J. Am. Chem. Soc.* 102 (1980)

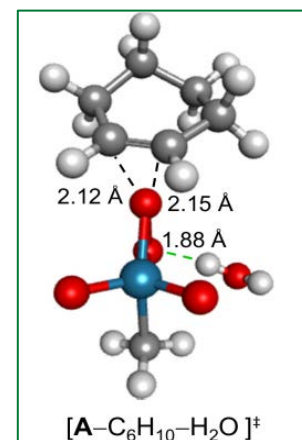
Semi-classical proton tunneling corrections Γ_i and experimental H₂O concentration included in reported thermodynamic and activation parameters

B. R. Goldsmith, T. Hwang, S. Seritan, B. Peters, S. L. Scott, *J. Am. Chem. Soc.* 137 (2015)

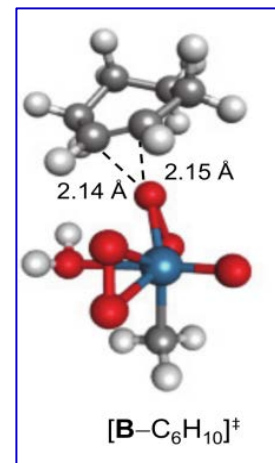
Cyclohexene epoxidation: Experiments and theory indicate that water only weakly accelerates the kinetics



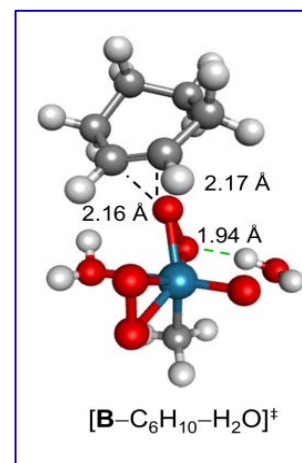
$$\Delta G^\ddagger = 118 \text{ kJ mol}^{-1}$$



$$\Delta G^\ddagger = 115 \text{ kJ mol}^{-1}$$

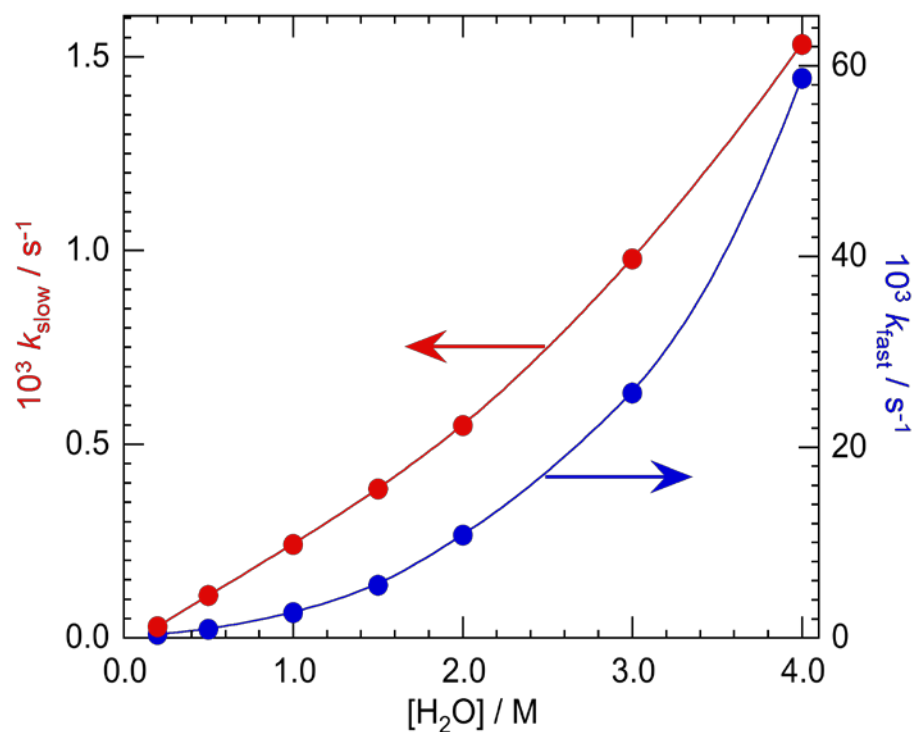
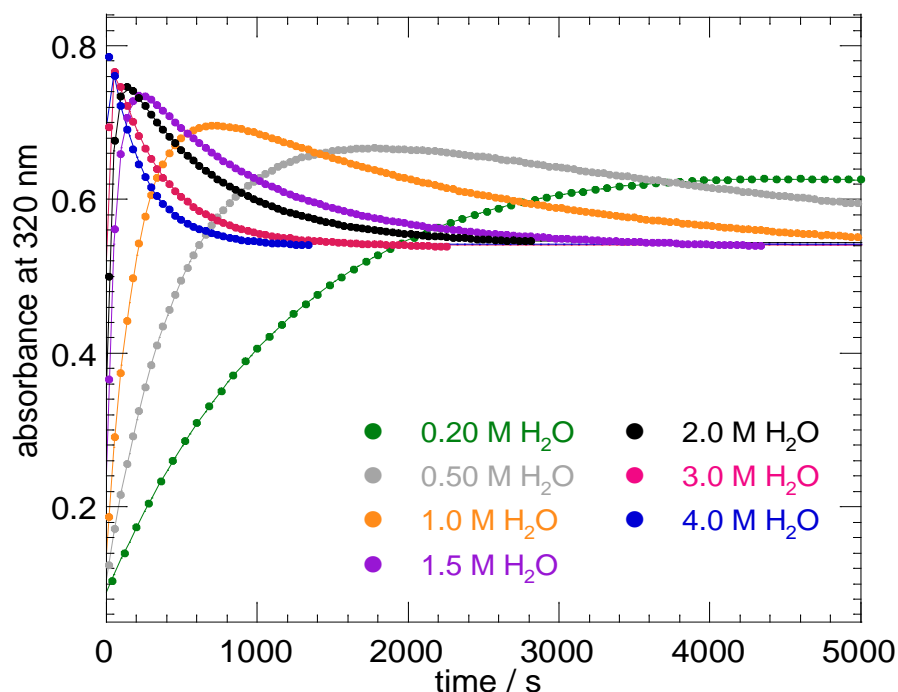
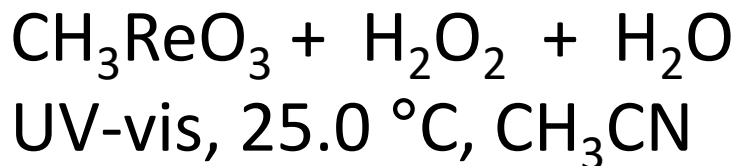


$$\Delta G^\ddagger = 96 \text{ kJ mol}^{-1}$$



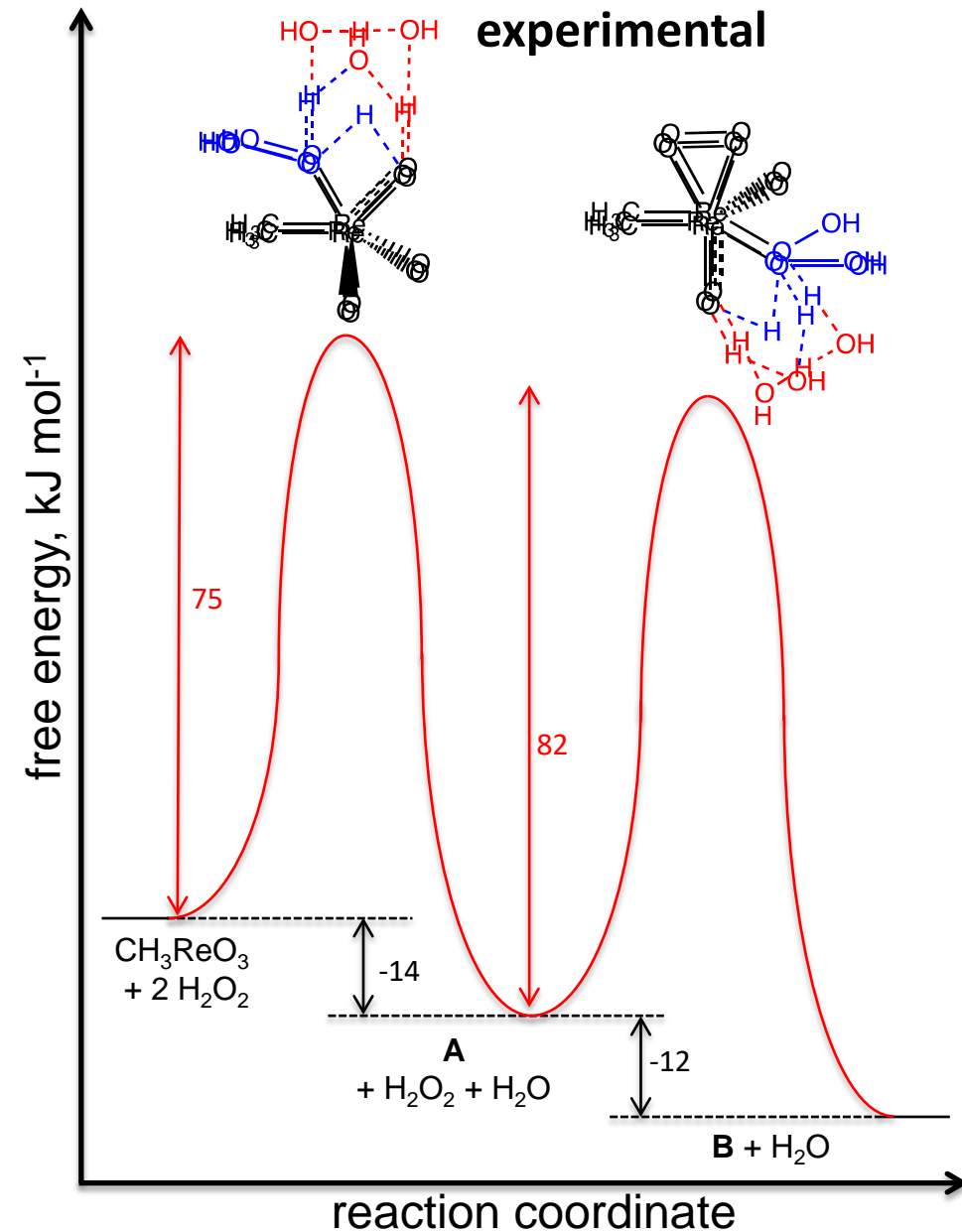
$$\Delta G^\ddagger = 94 \text{ kJ mol}^{-1}$$

UV-vis experiments suggest water dramatically accelerates the formation of peroxo complexes **A** and **B**

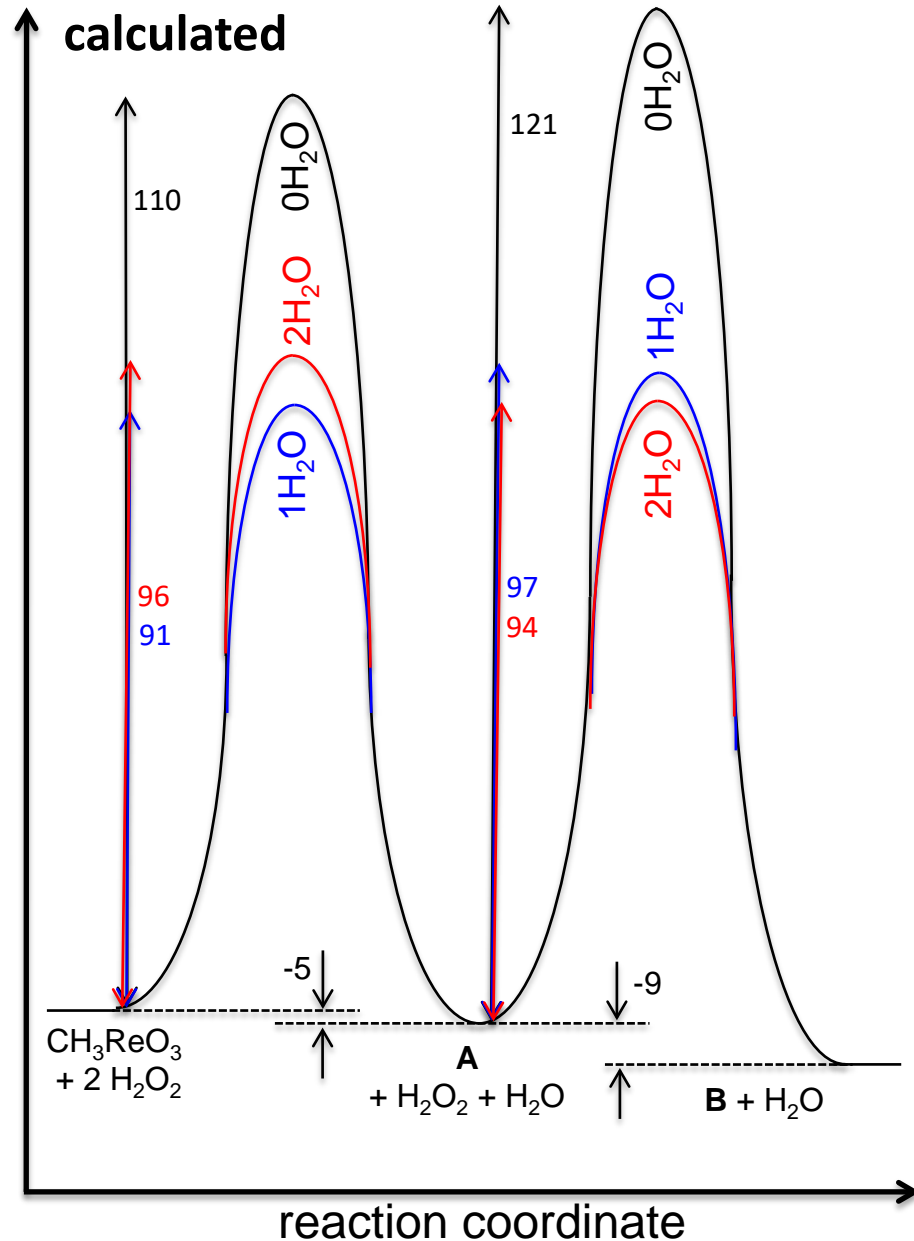


$$A_t = A_\infty + \alpha(1 - e^{-k_{\text{fast}}t}) + \beta e^{-k_{\text{slow}}t}$$

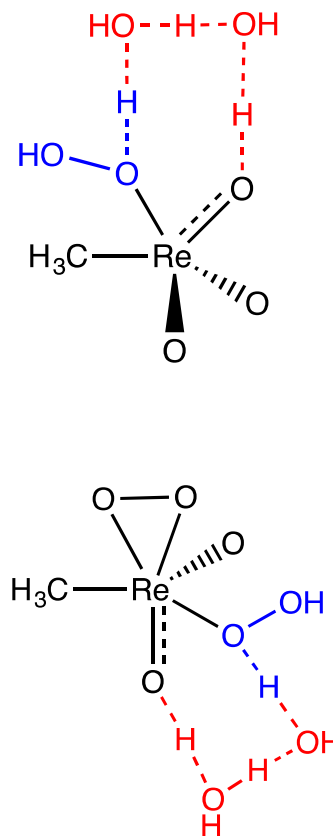
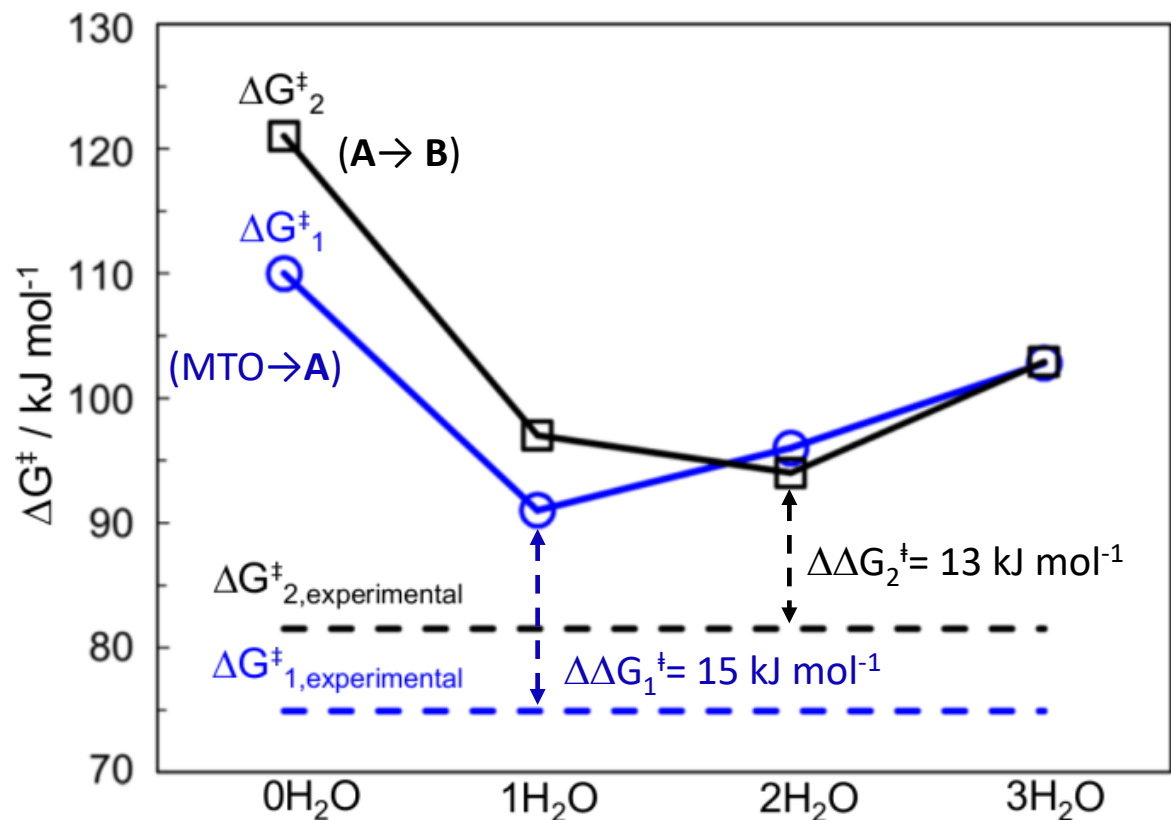
Free energy profiles for the formation of **A** and **B**



Initial rate predictions too slow
by 8 orders of magnitude!



Activation free energy for the formation of **A** and **B** vs. number of water in the transition states



“linearity of H-bonds in the transition state balances the entropic penalty of bringing four molecules together”

Proton inventory suggests two waters participating on average during peroxo complex formation

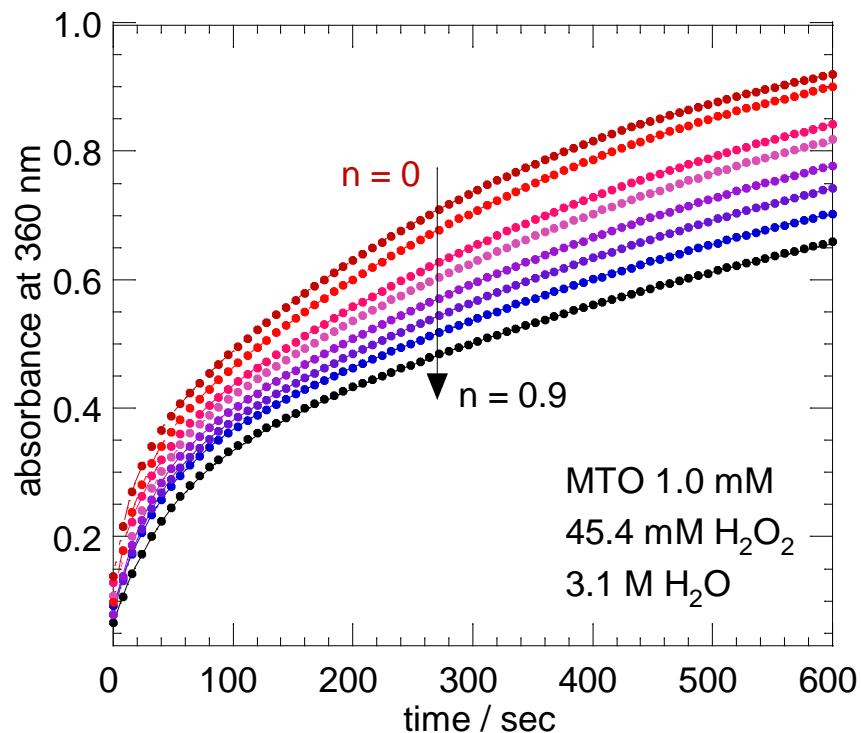
Measure solvent isotope effect on reaction kinetics

Keep $[\text{H}_2\text{O} + \text{D}_2\text{O}]$ constant

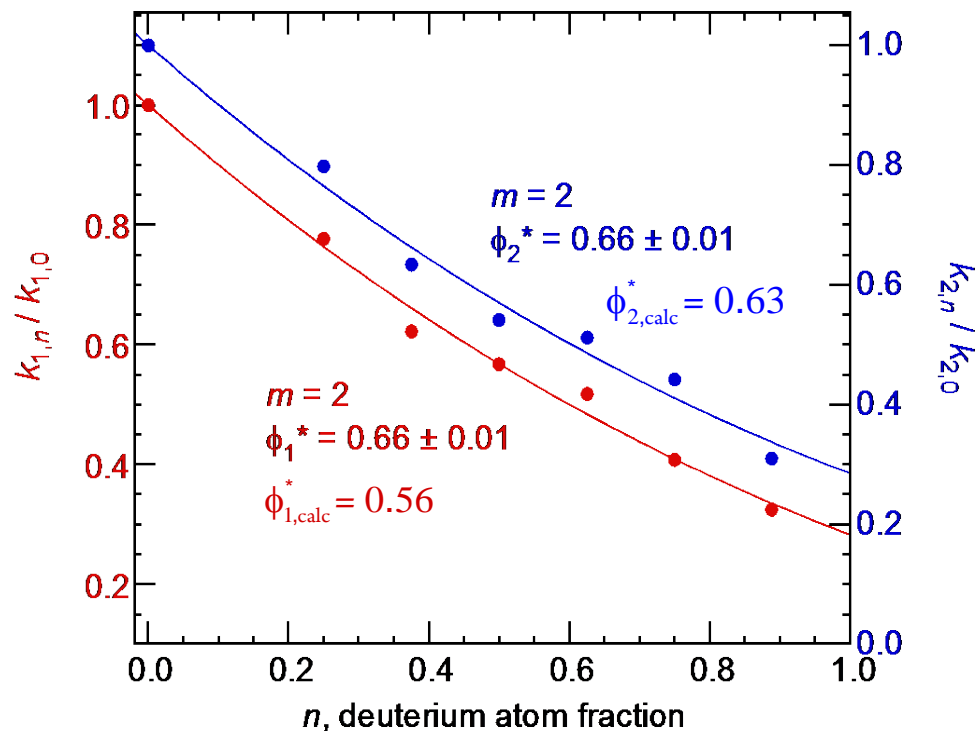
$m = \#$ of water molecules in transition state

$$k_n / k_0 = (1 - n + n\phi^*)^{m+1}$$

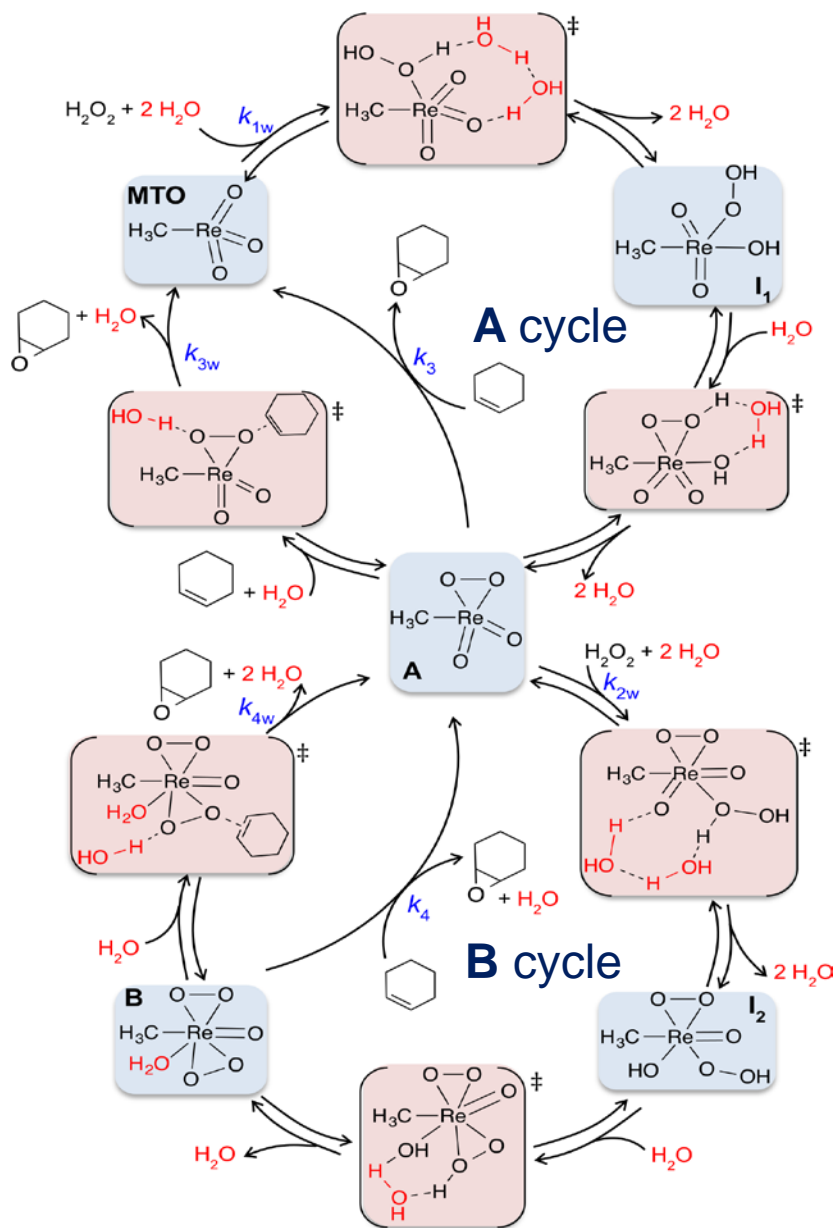
Vary mole fraction of D_2O



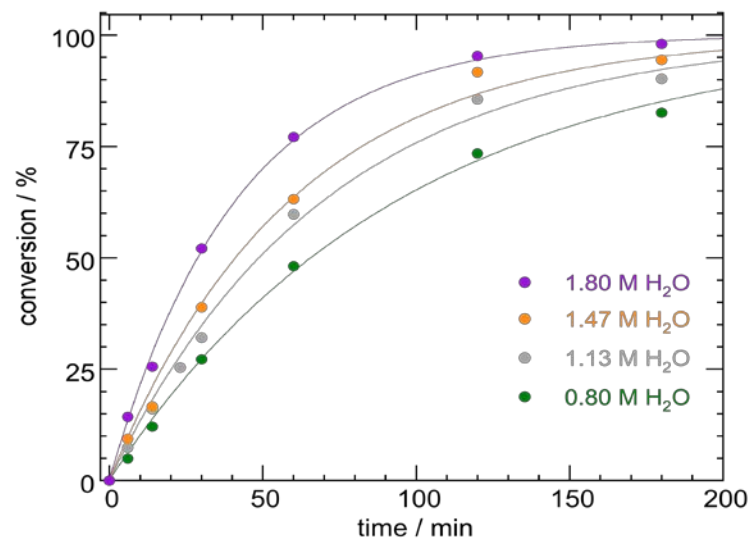
Experimental proton inventory



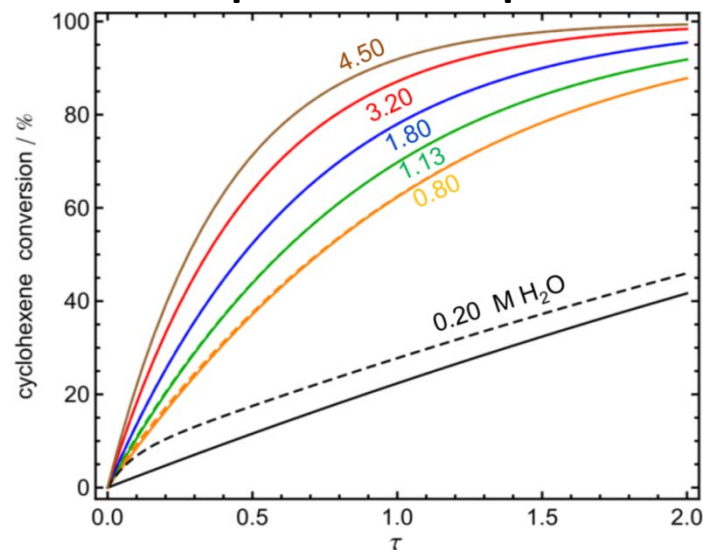
The full catalytic cycle and the roles of water



experimental kinetic profiles



computed kinetic profiles



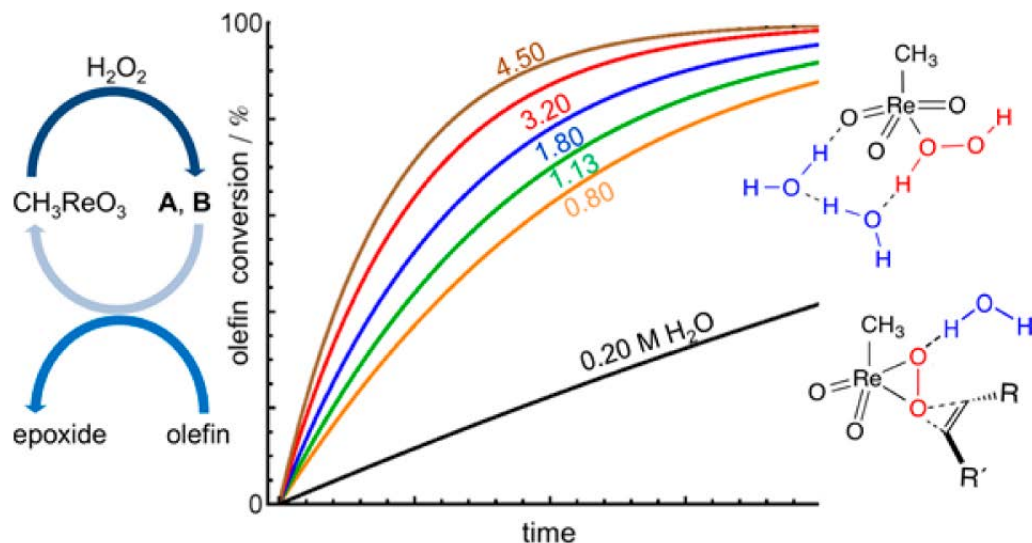
B. R. Goldsmith, T. Hwang, S. Seritan, B. Peters, S. Scott, *J. Am. Chem. Soc.* 137 (2015)

T. Hwang*, B. R. Goldsmith*, B. Peters, S. L. Scott, *Inorg. Chem.* 52 (2013)

Careful benchmarking between experiment and theory can lead to new insight that is both explanatory and predictive

**Thermodynamic and activation parameters
for all key steps fully characterized via both theory & experiment**

- ✓ calc. $\Delta G_1 \approx \text{exp. } \Delta G_1$
- ✓ calc. $\Delta G_2 \approx \text{exp. } \Delta G_2$
- ✓ calc. $\Delta G_1 < \Delta G_2$ (exp. $\Delta G_1 < \Delta G_2$)
- ✓ calc. $\Delta G_1^\ddagger \approx \text{exp. } \Delta G_1^\ddagger$
- ✓ calc. $\Delta G_2^\ddagger \approx \text{exp. } \Delta G_2^\ddagger$
- ✓ Similarly for ΔH_i^\ddagger and ΔS_i^\ddagger



**On average two H_2O participate
in the rate-determining transition states**

Strong water dependence is anticipated for other MTO-catalyzed oxidations
e.g., oxidation of alkenes, alkynes, aldehydes, ketones,
amines, sulfides, phosphines, and arenes

Acknowledgements

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Fritz Haber Institute,
Theory Department



Advertisement: My upcoming presentations at AIChE

Poster: **“Role of van der Waals and entropy on gold cluster (meta)stability”**

Comp. Mol. Sci. Eng. Forum, Monday

Talk: **“Local pattern discovery for uncovering structure-property relationships of materials”**

Data Min. Mach. Learn. Mol. Sci., Friday