

Rate-Enhancing Roles of Water Molecules in Methyltrioxorhenium-Catalyzed Olefin Epoxidation by Hydrogen Peroxide

Bryan R. Goldsmith, Taeho Hwang, Stefan Seritan, Baron Peters, Susannah L. Scott

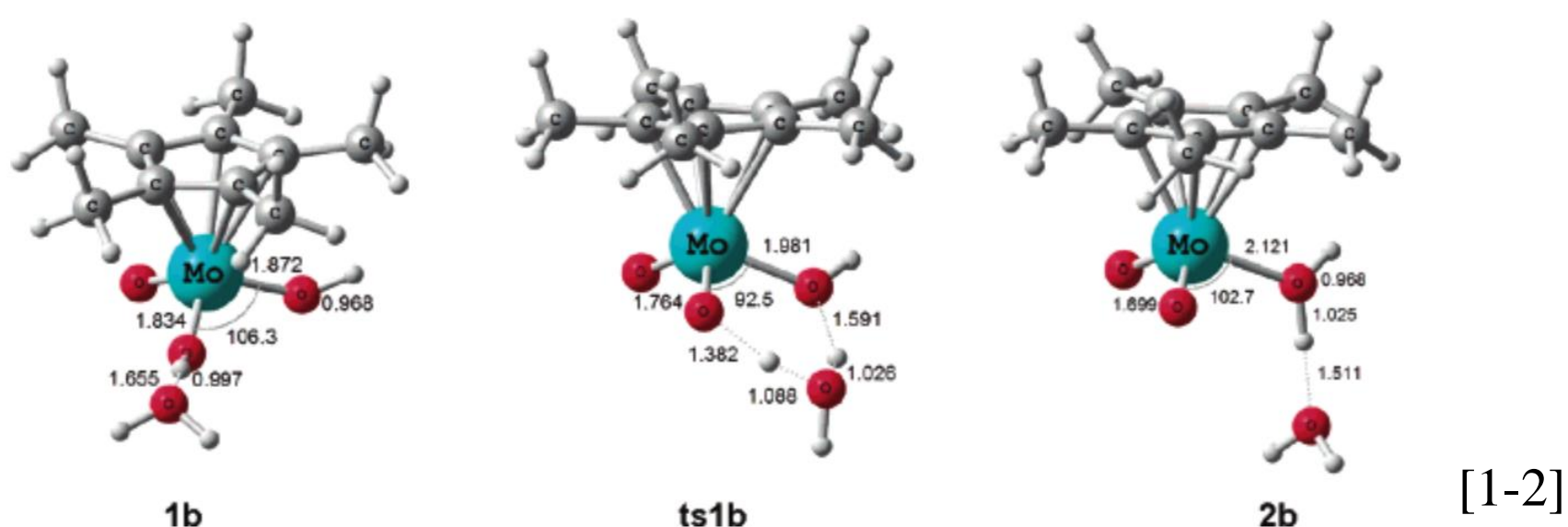


Department of Chemical Engineering, University of California, Santa Barbara, CA, 93106-5080
Department of Chemistry & Biochemistry, University of California, Santa Barbara, CA 93106-9510



The H₂O-dependence of MTO-catalyzed epoxidation has not been explained

Elucidating the origin of dramatic solvent effects is critical to being able to model solution-phase reactions



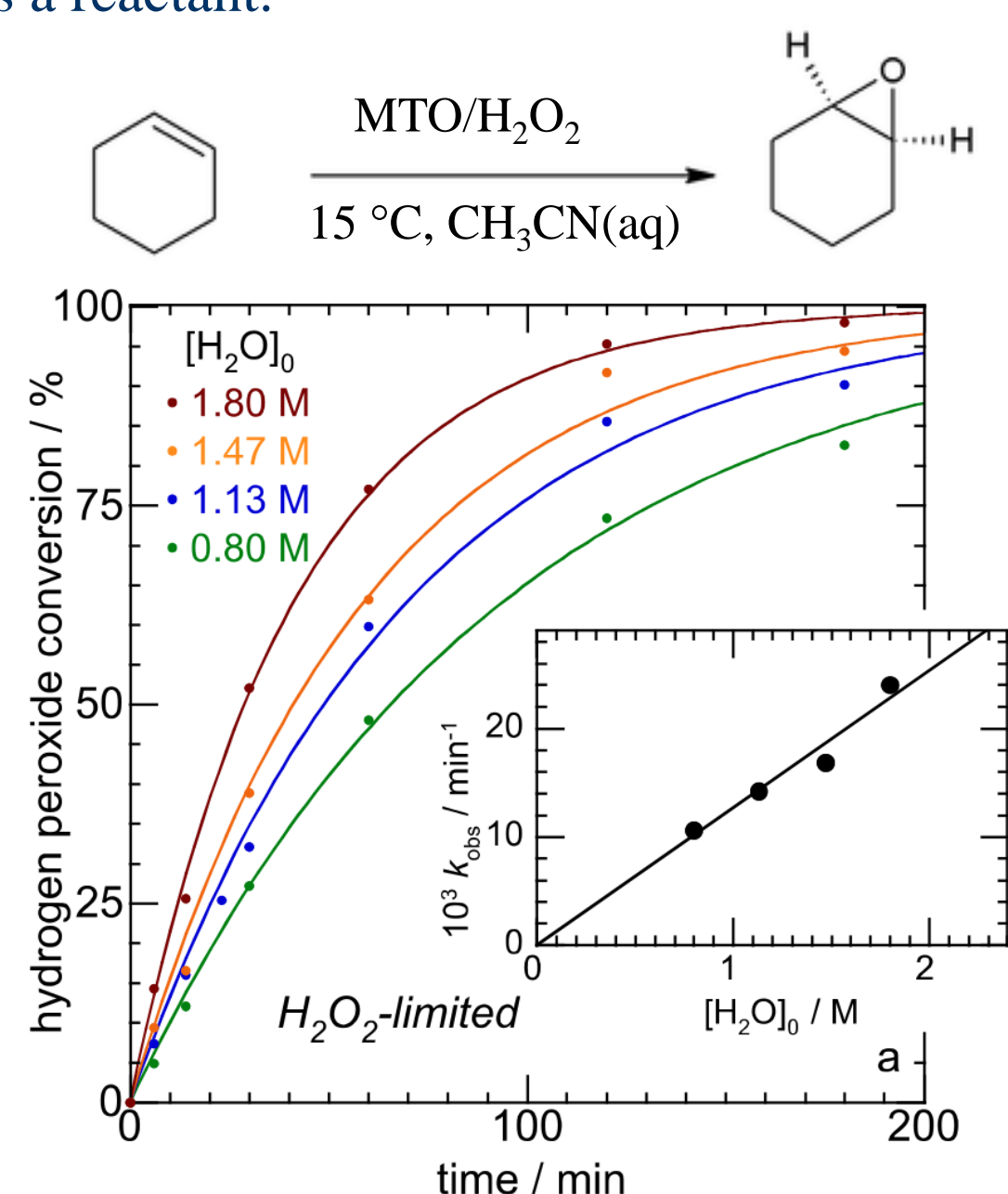
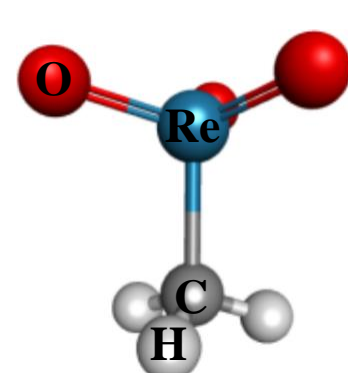
Methyltrioxorhenium-catalyzed epoxidation by H₂O₂ shows strong non-linear water acceleration effects, even though no step in the catalytic cycle explicitly requires water as a reactant.

Methyltrioxorhenium (CH₃ReO₃, MTO)

First organometallic Re oxide synthesized^[3]

The remarkable water-dependence has yet to be explained

Active catalyst for many reactions
Primarily for olefin metathesis and oxygen atom transfer reactions



We use experimental kinetic measurements, kinetic simulations, and DFT to explore the participation of water in MTO-catalyzed olefin epoxidation.

We address:

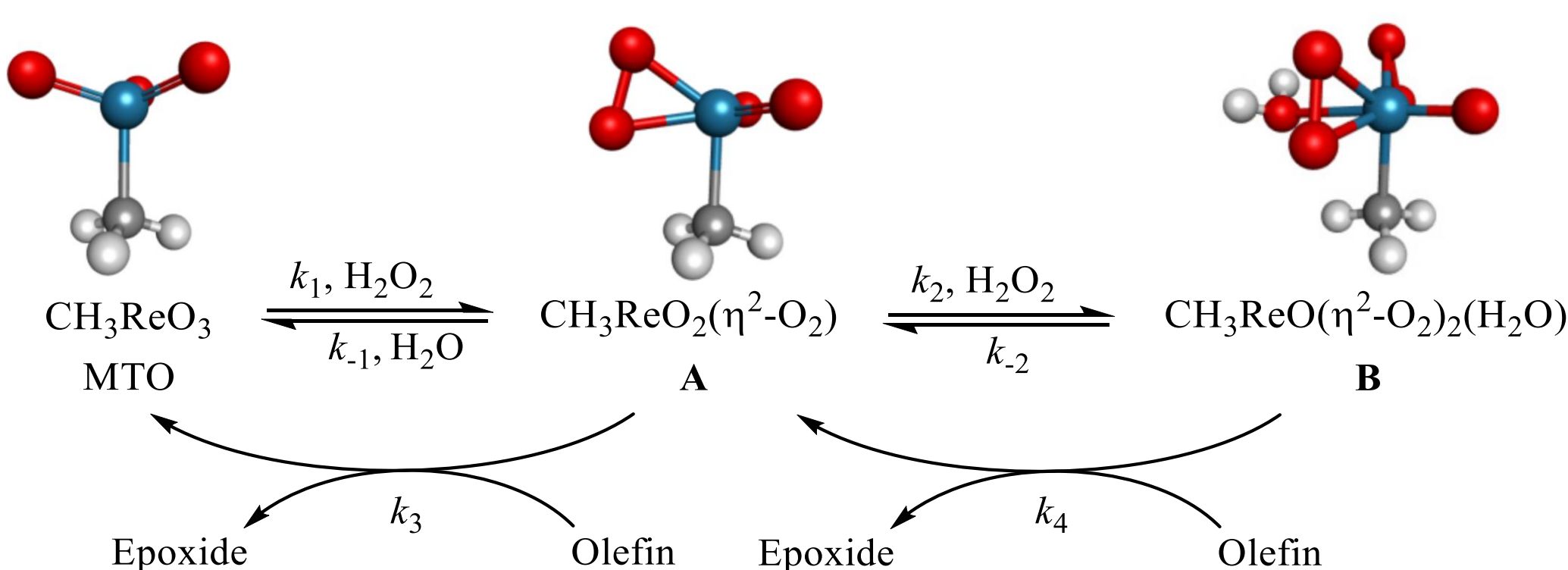
- The relative magnitudes of the rate enhancements due to water, in the epoxide formation steps vs. the peroxide activation steps;
- The relative importance of water-catalyzed and uncatalyzed pathways;
- The roles and precise numbers of water molecules involved in each step of the epoxidation catalytic cycle; and
- The extent to which DFT calculations, despite limitations in chemical accuracy, can predict and explain the observed kinetics of the complex solution-phase reaction involving multiple proton transfers

B. R. Goldsmith, T. Hwang, S. Seritan, B. Peters, and S. L. Scott, *J. Am. Chem. Soc.* 137, 9604 (2015)

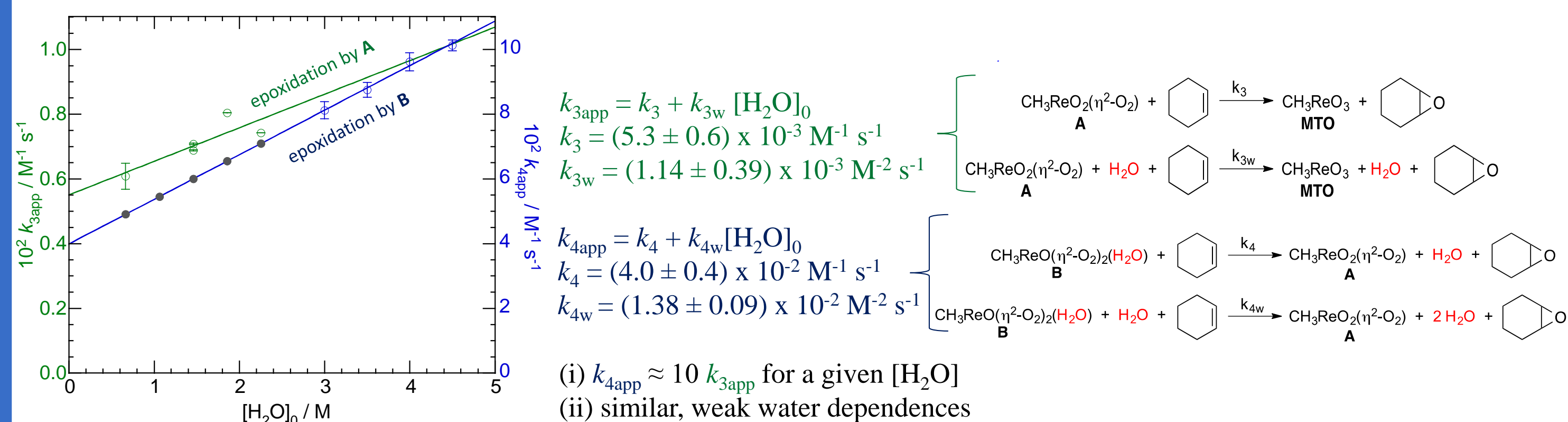
T. Hwang, B. R. Goldsmith, B. Peters, and S. L. Scott, *Inorg. Chem.* 52, 13904 (2013)

MTO-catalyzed olefin epoxidation

Methyltrioxorhenium activates H₂O₂ for oxygen atom transfer.^[4,5]



Experiments find that water accelerates the epoxidation steps only weakly



- $k_{4app} \approx 10 k_{3app}$ for a given $[H_2O]$
- similar, weak water dependences

DFT corroborates with experiments that water accelerates the epoxidation steps only weakly

Transition state description	Experiment	[H ₂ O] / M	ΔG [‡] Calculated
A + C ₆ H ₁₀ → [A-C ₆ H ₁₀] [‡]		2	118
		4	118
		8	118
A + H ₂ O + C ₆ H ₁₀ → [A-C ₆ H ₁₀ -H ₂ O] [‡]	82	116	115
		114	114
B + C ₆ H ₁₀ → [B-C ₆ H ₁₀] [‡]		96	96
		96	96
B + C ₆ H ₁₀ → [B'-C ₆ H ₁₀] [‡] + H ₂ O	77	99	100
		102	102
B + H ₂ O + C ₆ H ₁₀ → [B-C ₆ H ₁₀ -H ₂ O] [‡]		97	96

Free energy barriers are in kJ mol⁻¹ and reported at 15 °C

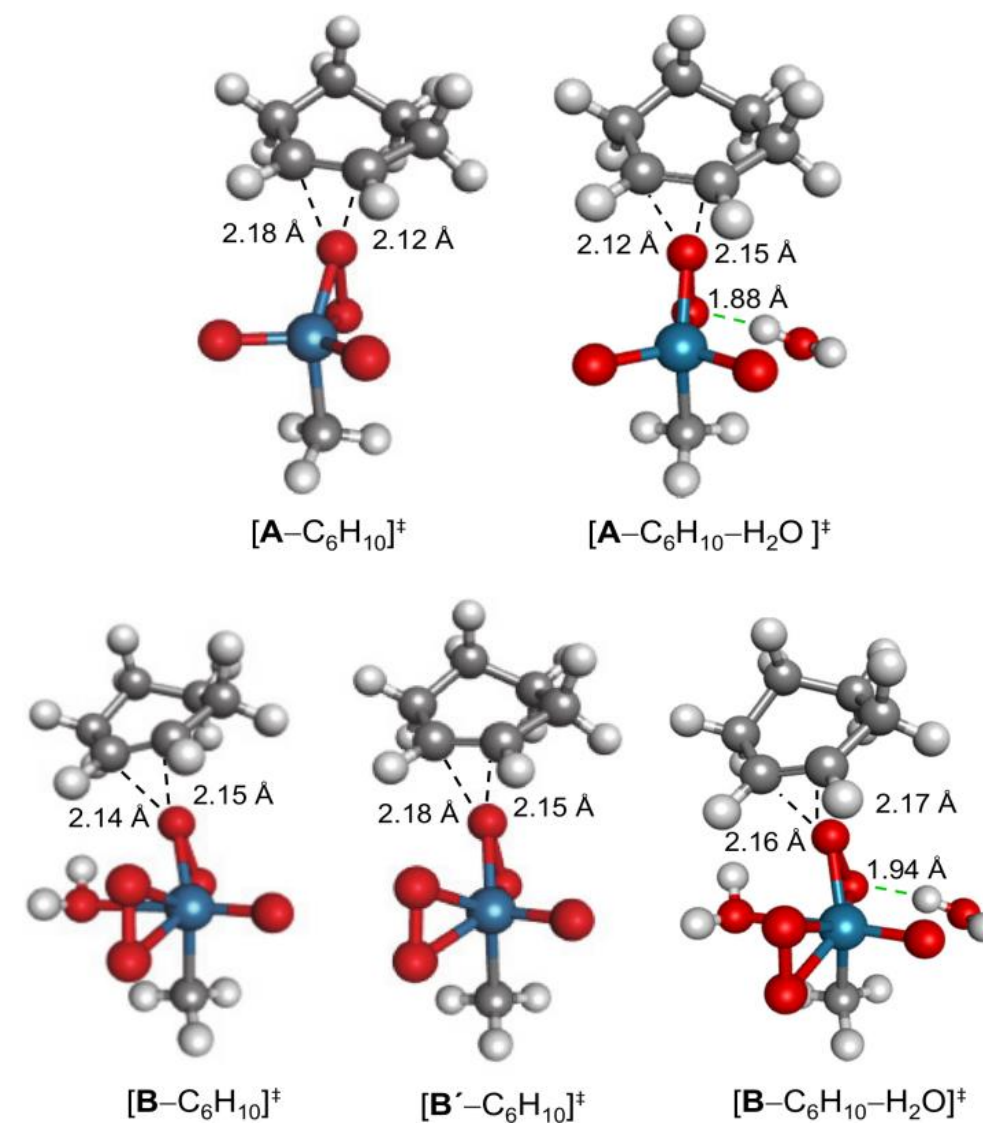
Level of theory; ωB97X-D/aug,def2-TZVP

Explicit/Implicit solvent; Conducting-type polarized continuum model (CPCM, solvent=acetonitrile)

Enthalpic interactions due to explicit waters present in each step (either 0, 1, 2, 3 H₂O)

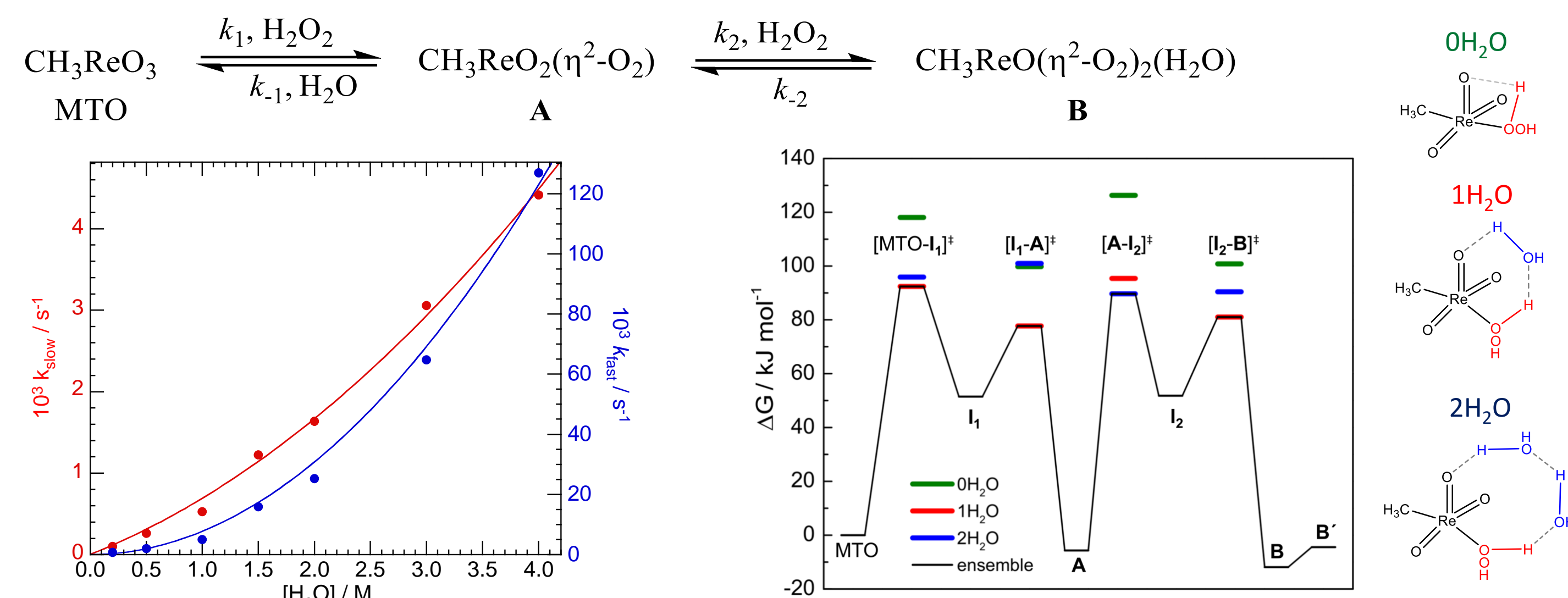
Wertz entropy correction used to account for structural correlations due to solvation in acetonitrile

Apparent Free energies; include zero point, rotation, translation, vibrations, proton-tunneling, and [H₂O].



H₂O strongly affects the rates at which the peroxo complexes are regenerated

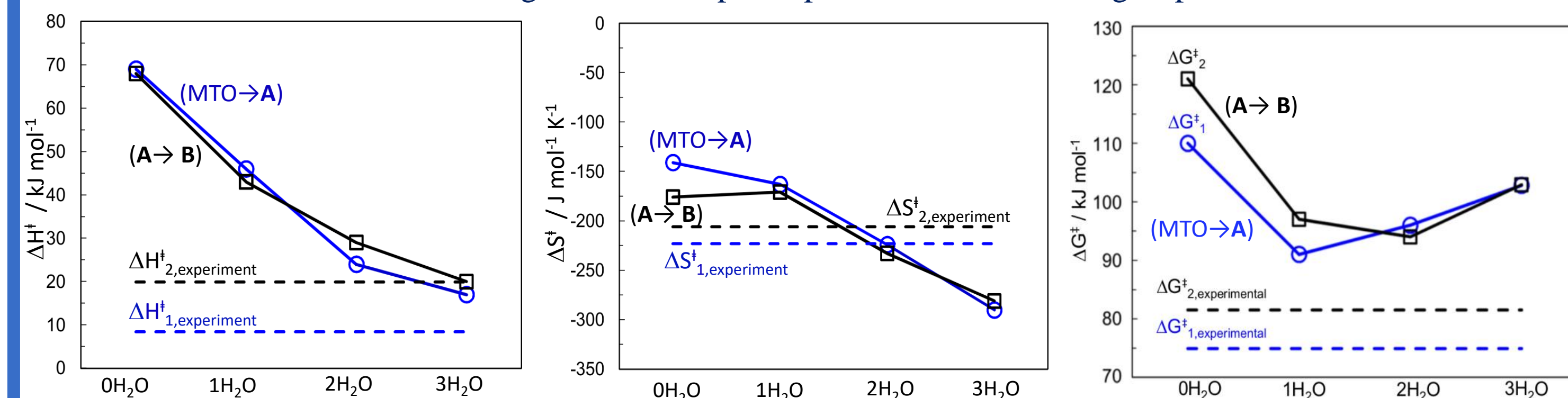
Strong water acceleration for regeneration of peroxo complexes A and B



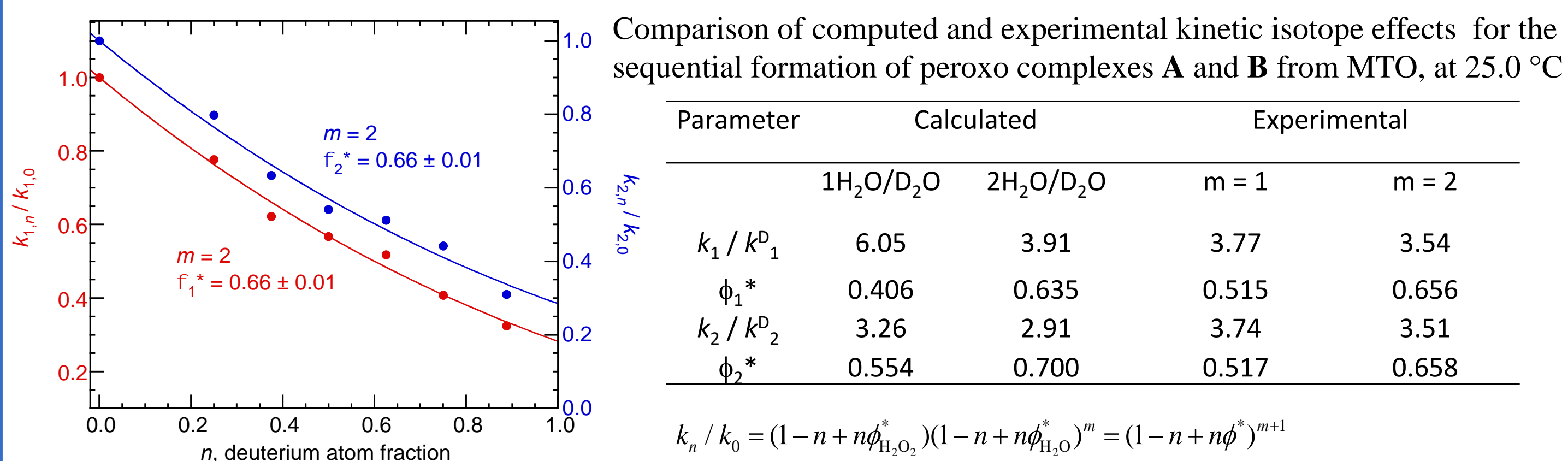
Water dependence of the measured pseudo-first-order rate constants k_{fast} (blue points) and k_{slow} (red points) for the reaction of 1.0 mM MTO with 49.1 mM H₂O₂ in aqueous CH₃CN at 25.0 °C. The curvefits (lines) correspond to a second-order dependence on $[H_2O]$ (for k_{fast}) and a mixed first- and second-order dependence on $[H_2O]$ (for k_{slow}).

Computed free energies for formation of the peroxo complexes of MTO. Transition states are identified by a hyphen between the reactant and product states of the Re complex. Solid green, red, and blue lines show free energies with 0H₂O, 1H₂O, and 2H₂O-assisted transition states.

On average two waters participate in rate-determining steps



Computed apparent activation parameters for the formation of the peroxo complexes A (blue circles) and B (black squares), via transition states involving different numbers of water molecules, compared to experimental values (dashed lines) measured at 25.0 °C with 2.0 M H₂O.



Final Remarks

Have described the full catalytic cycle and can quantitatively explain the effects of water

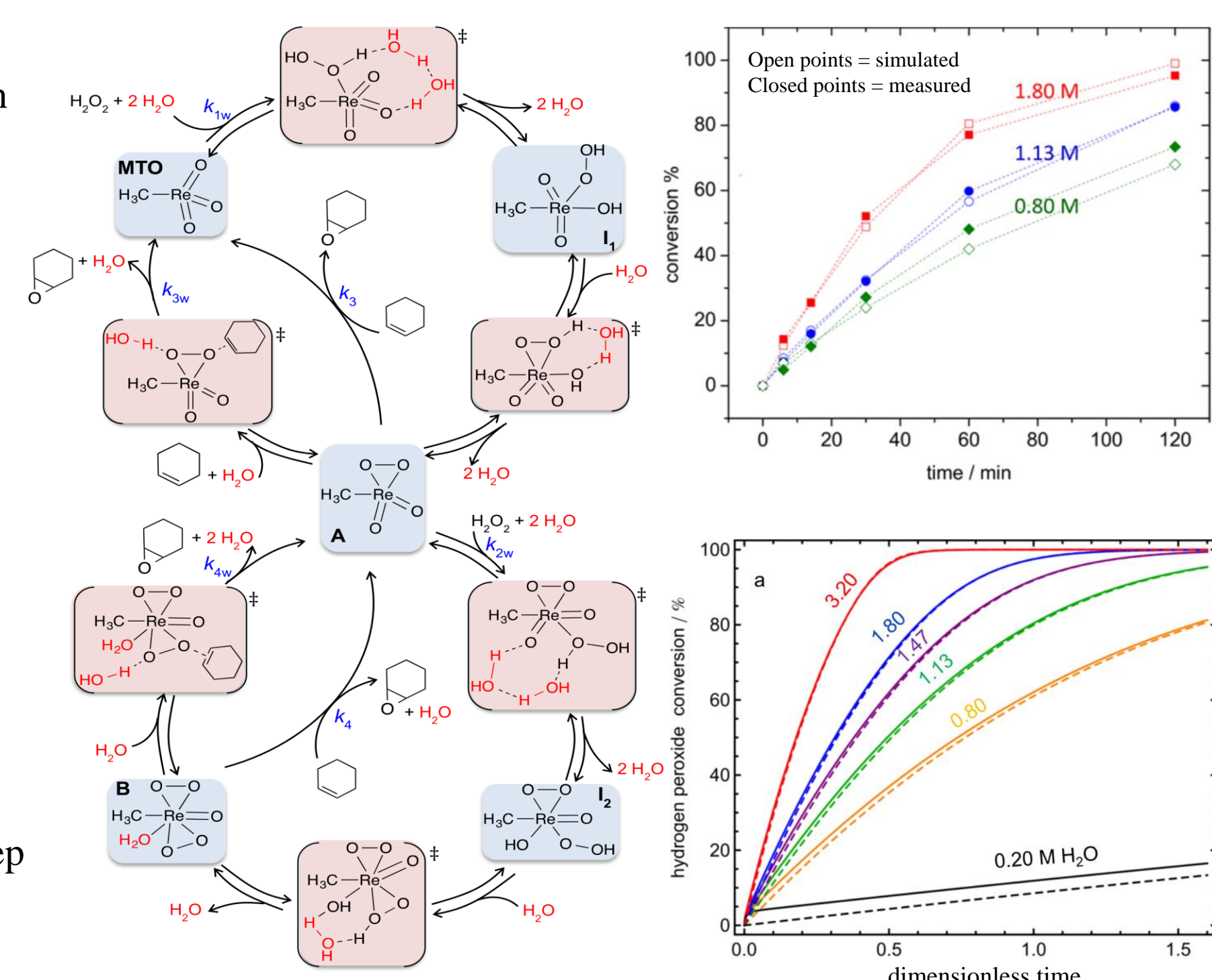
Strong water acceleration for regeneration of active peroxo-complexes

Weak water acceleration in epoxidation steps

Experimental measurements confirm water catalysis

Current modeling procedure adequately described complicated inorganic reaction in non-ideal solution

Water may also be an important component of the mechanism in other metal-catalyzed reactions for which proton transfer is a key step



Acknowledgments

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