



Quantitative Understanding of Advanced Oxidation Processes for the Treatment of Emerging Contaminants

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Outline

- ❖ Introduction to Advanced Oxidation Processes (AOPs)
- ❖ AOPs project
- ❖ Background and Objective
- ❖ Linear Free Energy Relationships (LFERs)
- ❖ Approaches
- ❖ Results and Discussions





Introduction 1/2

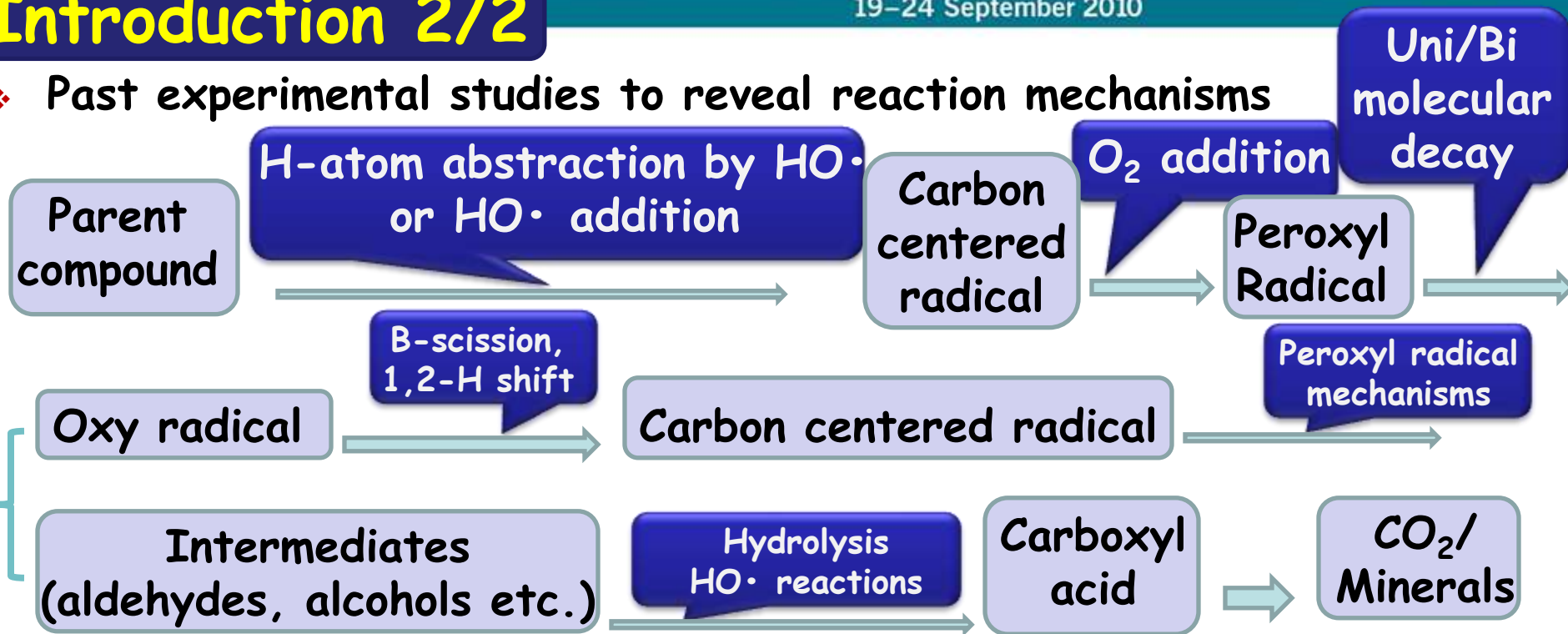
- ❖ Emerging contaminants: Detection of trace organic contaminants and uncertain human health and ecological effects
- ❖ Concern about emerging contaminants necessitate a task to assess their removal efficiency during water treatment
- ❖ Advanced Oxidation Processes (AOPs) are attractive and promising water treatment technologies because of the capability of mineralization of organic compounds.
- ❖ AOPs may be used to control the emerging contaminants.
- ❖ Non-selectivity of $\text{HO}\cdot$ and radical chain reactions make AOPs complex processes as well as diversity and complexity of structure of a large number of emerging contaminants.





Introduction 2/2

- ❖ Past experimental studies to reveal reaction mechanisms



- ❖ Development of first-principle based mechanistic models:

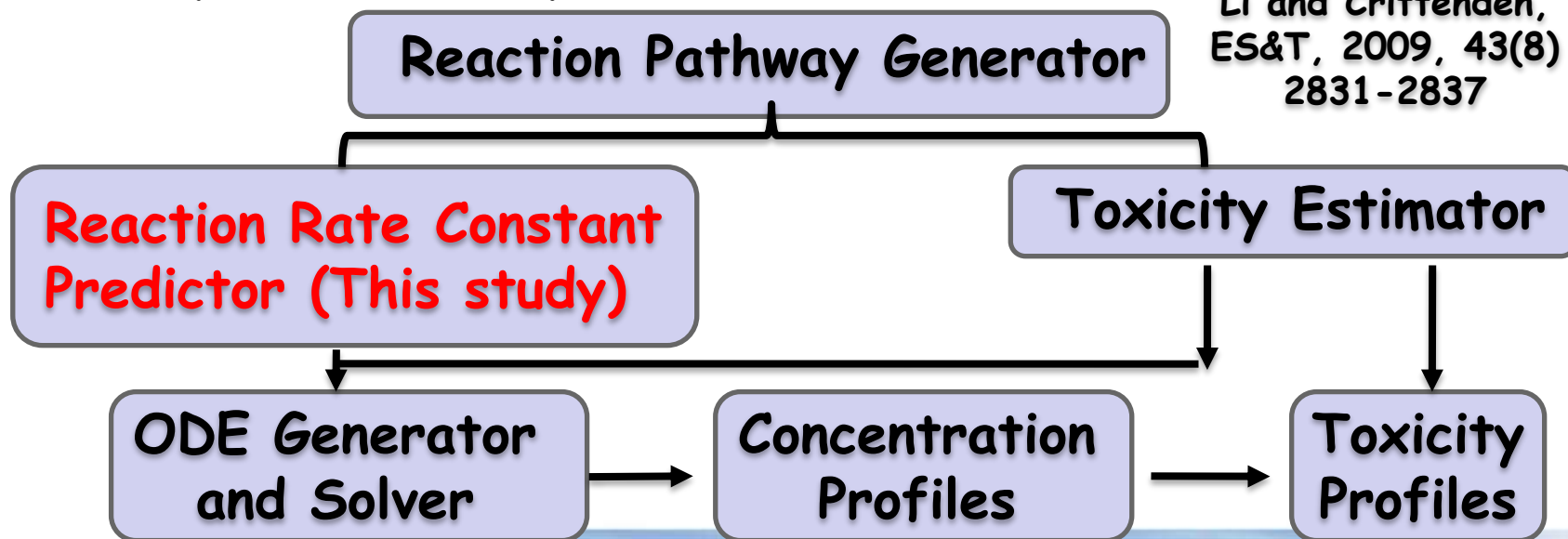
- ✓ To enumerate reaction pathway
- ✓ To calculate concentrations of intermediates and byproducts
- ✓ To estimate human health effects of intermediates and byproducts



AOP project

- ❖ Establish a computer-based kinetic model of reactions that are initiated by $\text{HO}\cdot$ in aqueous AOPs.
 - Reaction Pathway Generator (Graph theory)
 - Reaction Rate Constant Predictor (Quantum mechanical calculations)
 - Ordinary Differential Equations (ODEs) Solver

Li and Crittenden,
ES&T, 2009, 43(8)
2831-2837





Background

- ❖ Group Contribution Method (GCM) to predict aqueous phase HO \cdot reaction rate constants with wide range of functional groups
- ❖ Ab initio reaction rate constant predictors that consider reaction energy

*Minakata et al., 2009 ES&T, 43,6220–6227

Objective

- ❖ To develop a Linear Free Energy Relationships (LFERs) that bridge kinetics with thermochemical property for HO \cdot reactions with neutral compounds

*Neutral (Minakata et al., 2010 ES&T submitted)

*Ionized compounds (Minakata et al., ES&T in preparation)





Linear Free Energy Relationship

$$\log_{10} k_I - \log_{10} k_R = -\rho \left(\Delta G_{\text{rxn},I}^{\text{act}} - \Delta G_{\text{rxn},R}^{\text{act}} \right) + \sigma$$

where

k_I and k_R are the reaction rate constants, $M^{-1}s^{-1}$, for an arbitrary reaction, I, and a reference reaction, R, respectively;

ρ denotes coefficients for the difference in the free energy of activation;

σ is a constant;

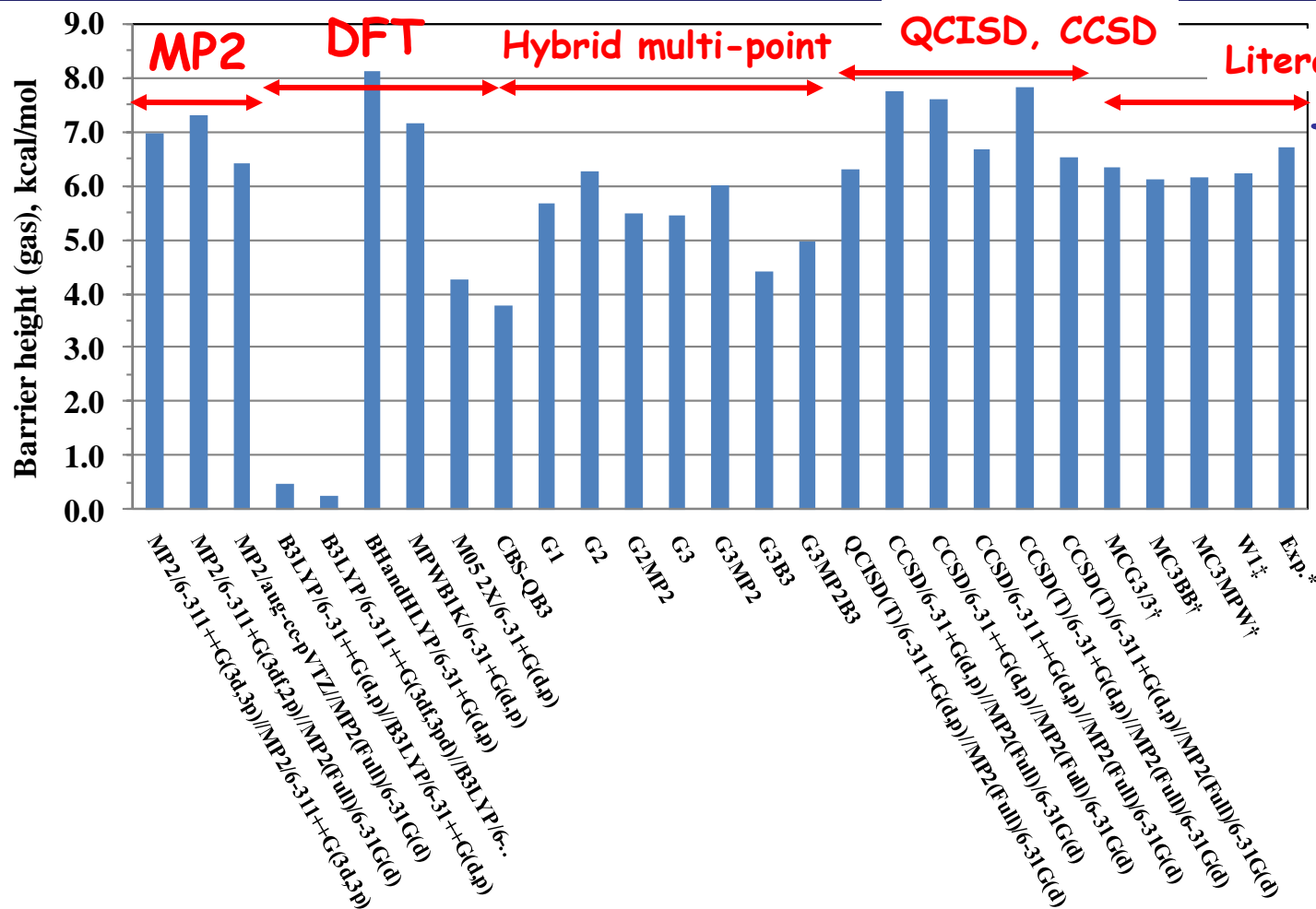
$\Delta G_{\text{rxn},I}^{\text{act}}$ and $\Delta G_{\text{rxn},R}^{\text{act}}$ are the free energies of activation, kcal/mol, for reactions I and R, respectively

$$\Delta G_{\text{rxn},\text{aq}}^{\text{act}} = \Delta G_{\text{rxn},\text{aq}}^{\neq} + \Delta G_{\text{extra}}$$

$$\left\{ \begin{array}{l} \Delta G_{\text{rxn},\text{aq}}^{\neq} = \Delta G_{\text{rxn},\text{gas}}^{\neq} + \Delta \Delta G_{\text{rxn},\text{solvation}}^{\neq} \\ \Delta G_{\text{extra}} = -RT \ln \gamma(T) \end{array} \right.$$

← Tunneling effect

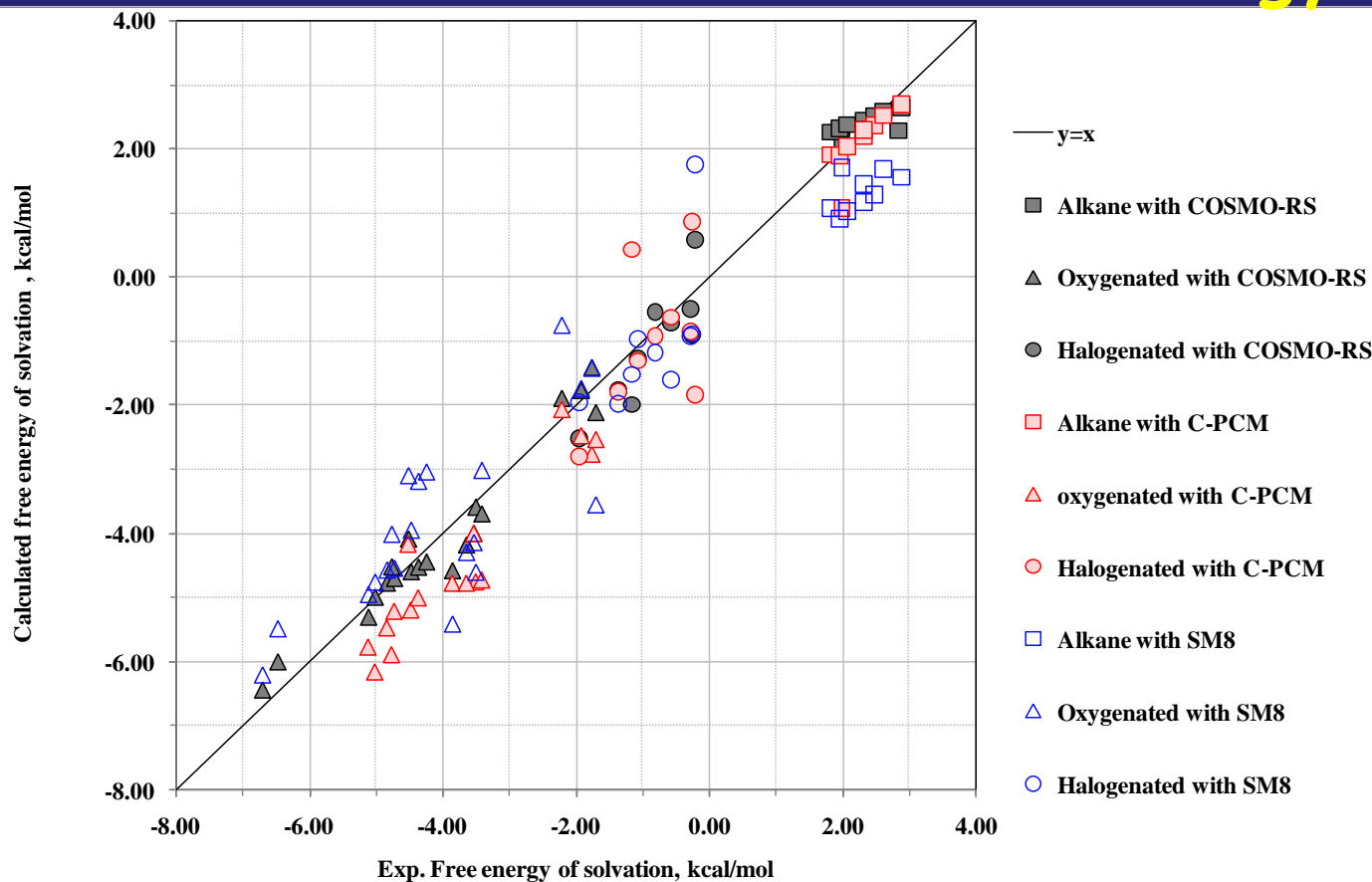
Results and Discussion: Gaseous Phase $\Delta G^\ddagger_{\text{rxn,gas}}$



WI: Boese and Martin, 2004,
MCG3/3: Ellingson, et al., 2009,
Estimate by exp: Lynch and Truhlar, 2001

- Hybrid multi-point energy method; Gaussian- n -series (G1, G2 and G3, (Pople et al., 1989; Curtiss et al., 1991;1998) should be promising in terms of computational demand and accuracy.
- G1, G2 and G3 have been verified with compounds with functional groups (CH_3OH , CH_3OCH_3 , CH_3COCH_3 , CH_3COOH , CH_3CHO , CH_3Cl).

Results and Discussion: Free Energy of Solvation



- **CPCM**
- **SM8**
- **COSMO-RS**

* $G_{\text{solv,exp}}^i$ is from Minnesota Solvation Database (Marenich et al., 2009)

	COSMO-RS with COSMOtherm	CPCM with G3B3 and UAHF radii	SM8 with M06-2X/6-31+G(d,p) and Bondi radii
N	40	38	39
SD	0.79	1.6	1.8

$$SD = \sqrt{\frac{1}{N-1} \sum_{i=1}^N \left(\frac{G_{\text{solv,exp}}^i - G_{\text{solv,calc}}^i}{G_{\text{solv,exp}}^i} \right)^2}$$

COSMO-RS showed better performance than **CPCM** and **SM8**, and has more realistic picture of solvation process in water.

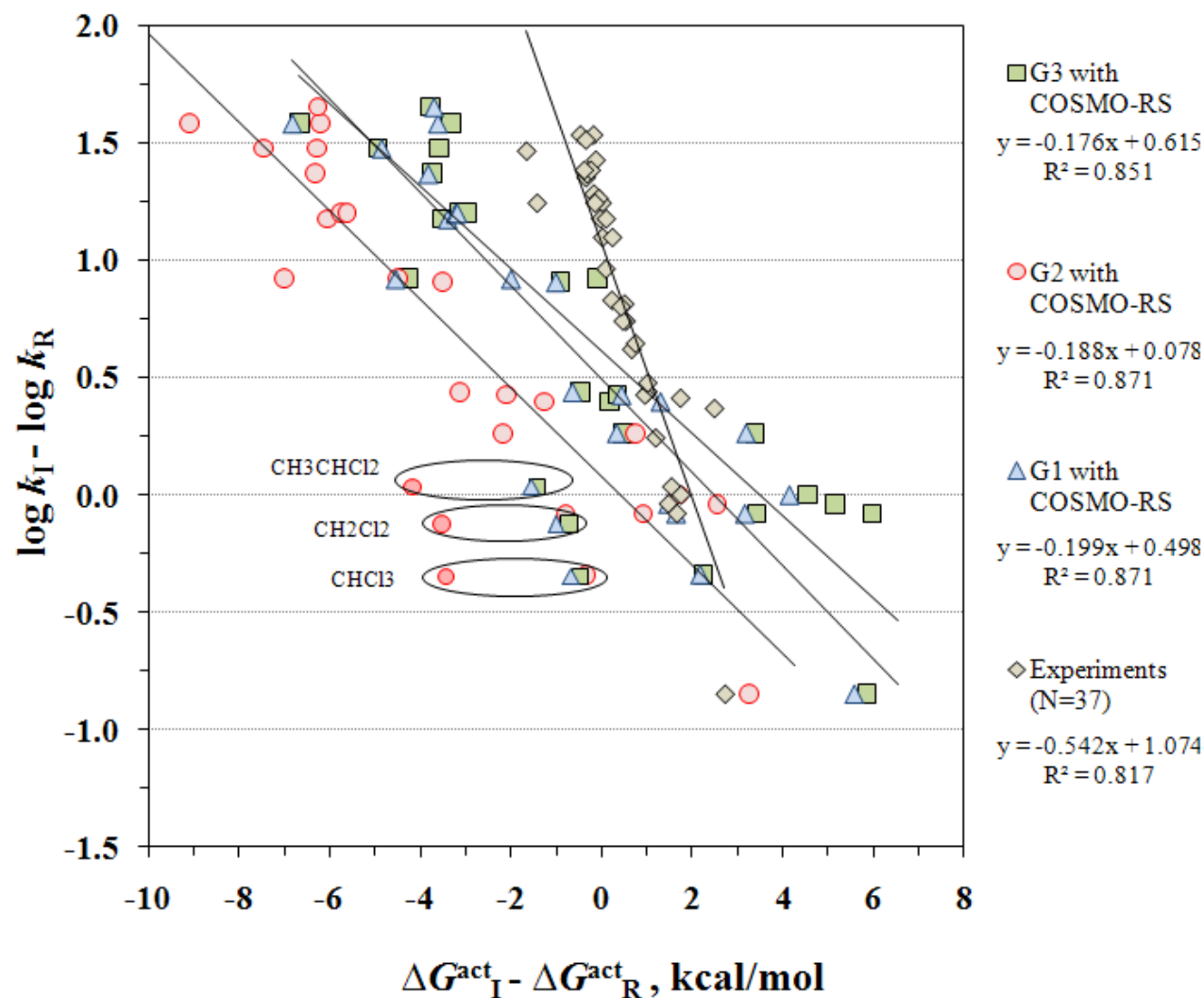


Approaches: LFERs

$$\Delta G_{\text{rxn, aq}}^{\neq} = \Delta G_{\text{rxn, gas}}^{\neq} + \Delta\Delta G_{\text{rxn, solvation}}^{\neq}$$

- Gaseous phase : G1, G2 and G3 methods in Gaussian03 (Frisch et al., 2003).
- Free energy of solvation: COSMO-RS theory in COSMOtherm.
- A change of state from 1 mol/24.47 L (gaseous phase 298 K) to 1 mol/L (aqueous phase 298 K) was included (i.e., 1.90 kcal/mol = $RT\ln(24.47)$).
- Among different transition states and conformers, the lowest energy of $\Delta G_{\text{gas}}^{\neq}$ was chosen to establish the LFERs.

LFERs for H-atom abstraction from a C-H bond by HO•



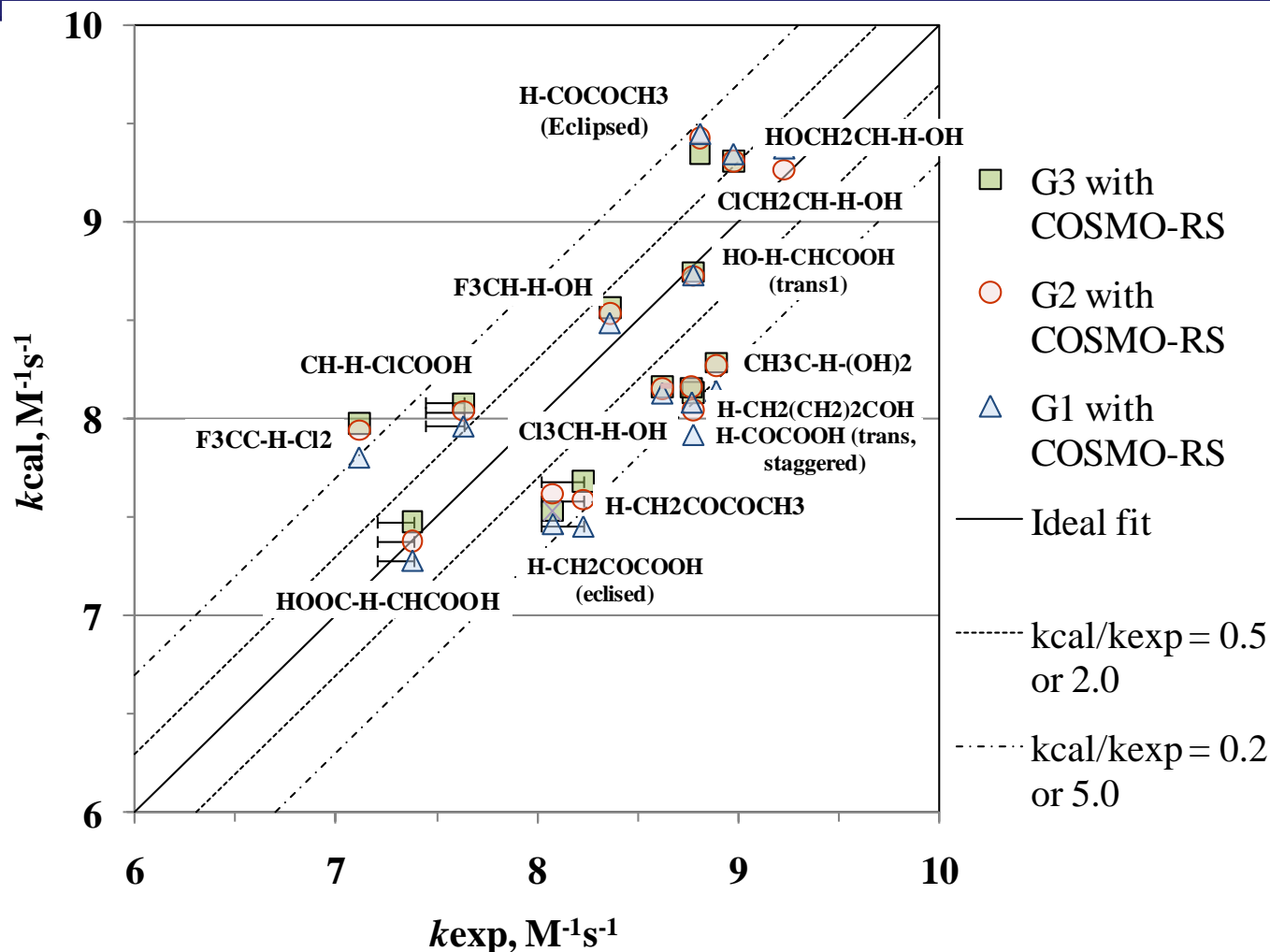
➤ 24 neutral compounds with single functional group

➤ Reaction of HO• with CH₄ is chosen as a reference reaction

➤ Calculated $\Delta G_{\text{rxn, aq}}^{\text{act}}$ is approximately ± 4 kcal/mol which is within the errors that arises from quantum mechanical calculation for gaseous phase

➤ Considering rate constant expression based on TST, 1 kcal/mol of difference in $\Delta G_{\text{rxn, aq}}^{\ddagger}$ causes 5.4 times difference in rate constant so, direct calculation of rate constant is not feasible.

Results and Discussion: Predicting $k_{HO\cdot}$



- 10 neutral compounds with multi-functional-groups
- Using the LFERs that are obtained from the calibration, predicting the $HO\cdot$ reaction rate constants for multi-functional-groups compounds indicates $0.2 < k_{pred}/k_{exp} < 5.0$.



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