



# 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

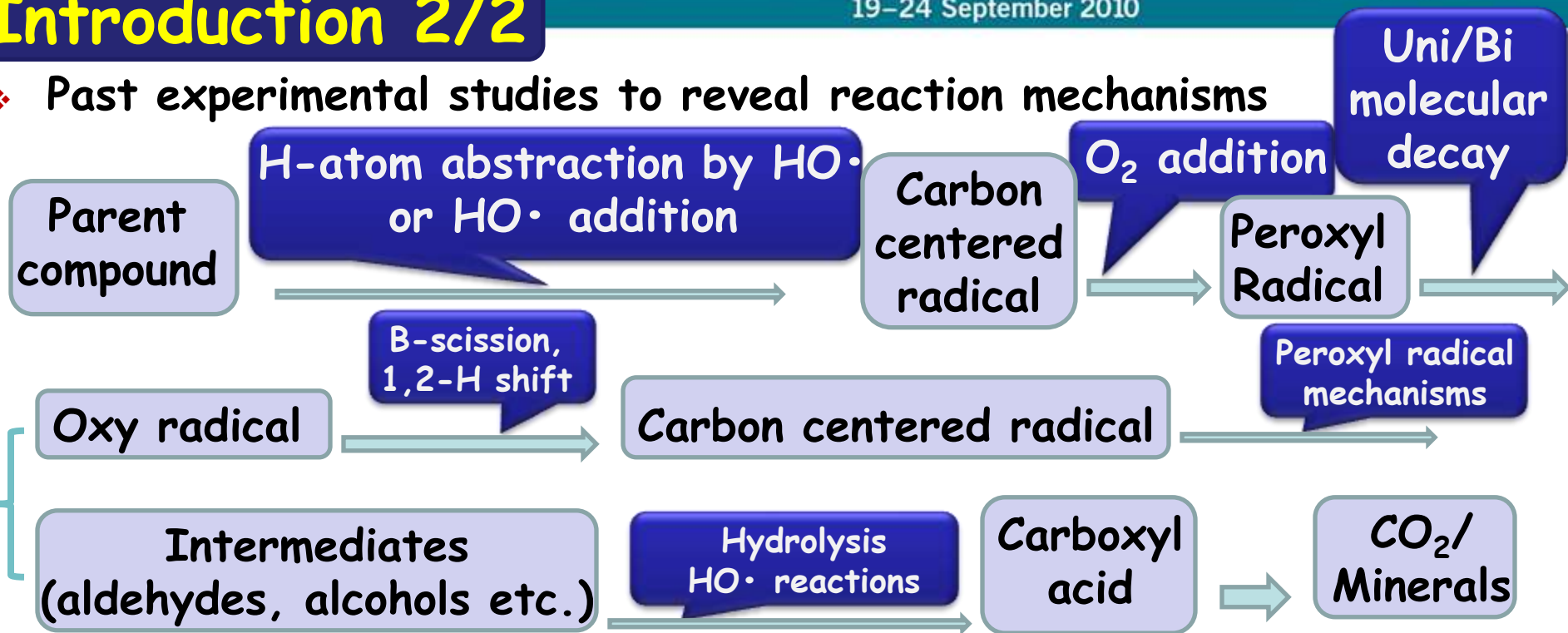
- ❖ Emerging contaminants: Detection of trace organic contaminants and uncertain human health and ecological effects
- ❖ Concern about emerging contaminants necessitate a task to assess their removal efficiency during water treatment
- ❖ Advanced Oxidation Processes (AOPs) are attractive and promising 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



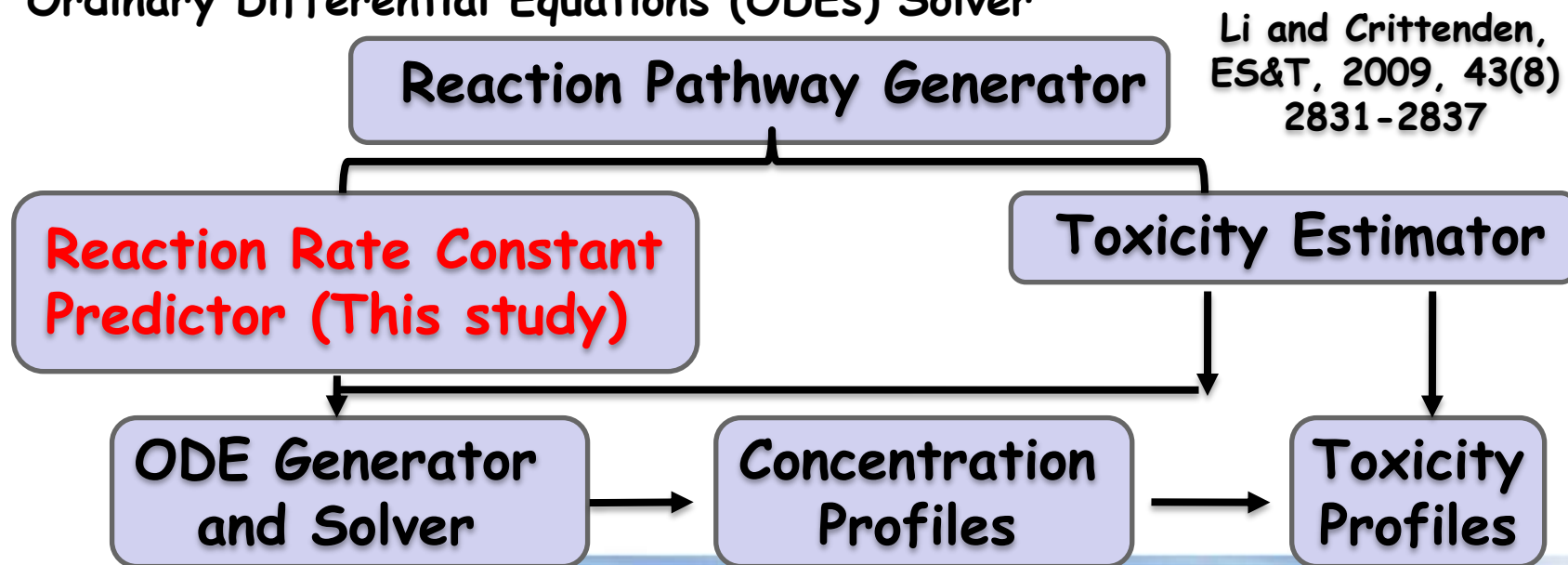
- ❖ **Development of first-principle based mechanistic models:**

- ✓ 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





## 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;

$\rho$  denotes coefficients for the difference in the free energy of activation;

$\sigma$  is a constant;

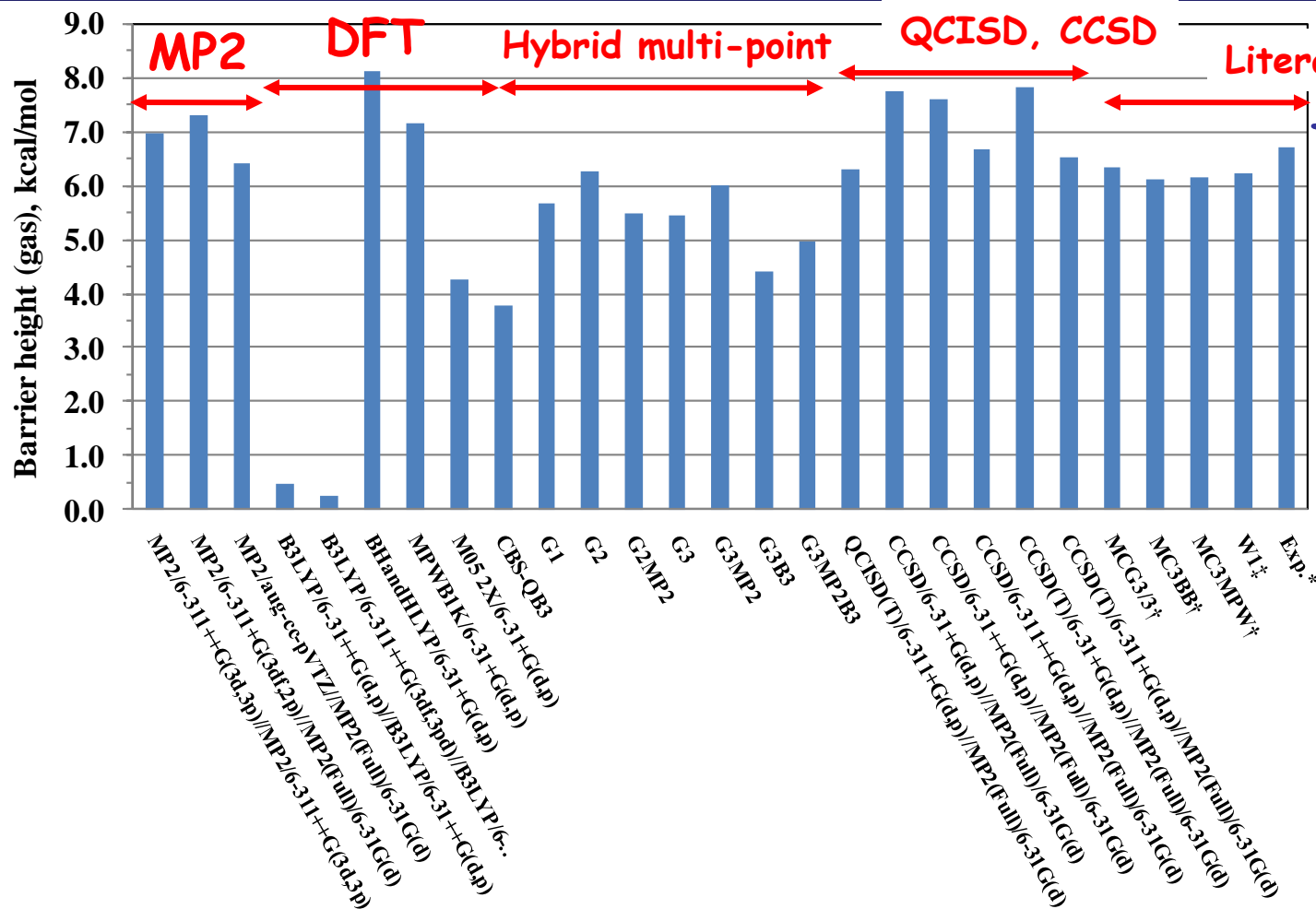
$\Delta G_{\text{rxn},I}^{\text{act}}$  and  $\Delta G_{\text{rxn},R}^{\text{act}}$  are the free energies of activation, kcal/mol, for reactions I and R, respectively

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

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

← Tunneling effect

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

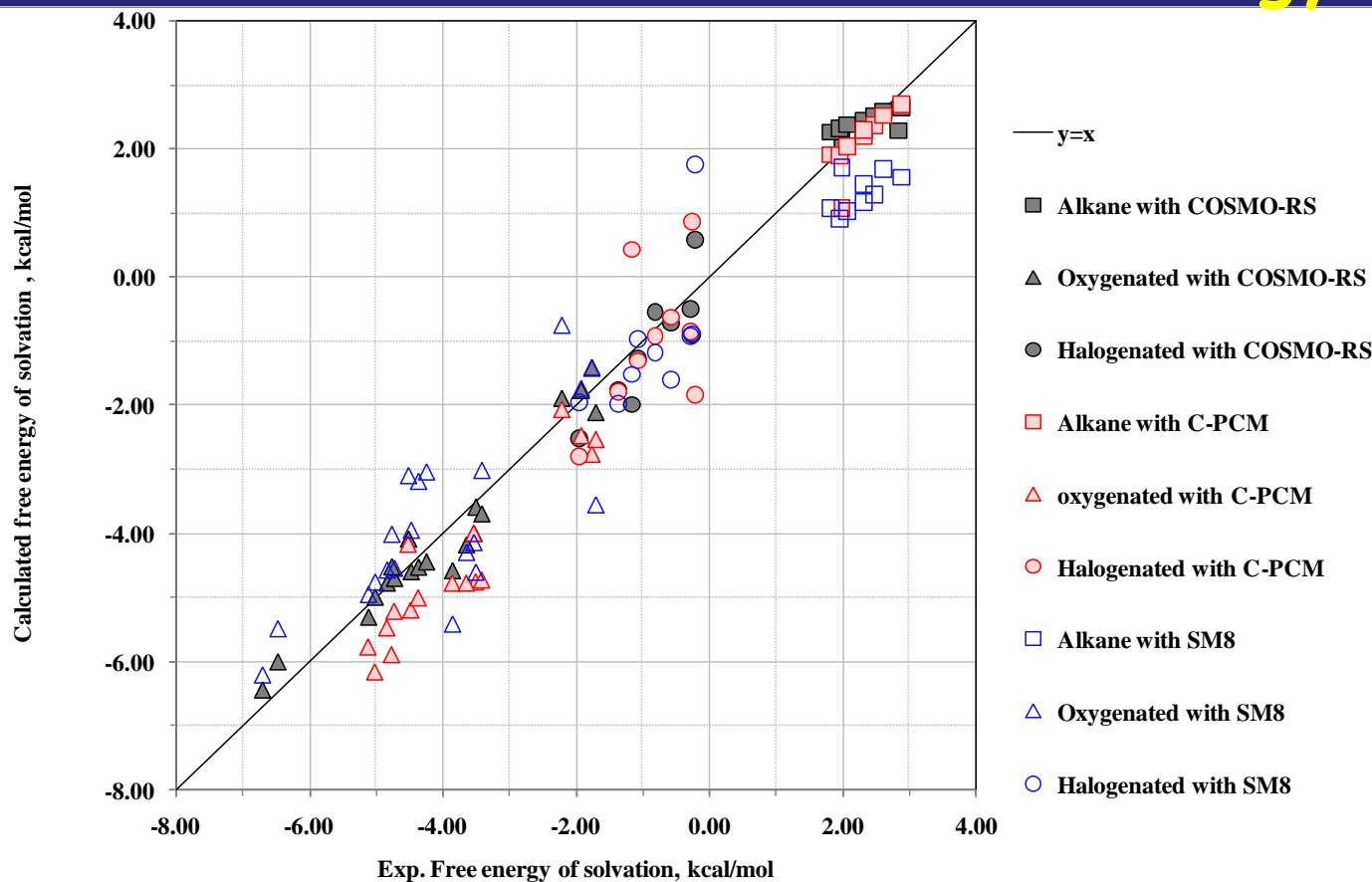


WI: Boese and Martin, 2004,  
MCG3/3: Ellingson, et al., 2009,  
Estimate by exp: Lynch and Truhlar, 2001

- 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 ( $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{OCH}_3$ ,  $\text{CH}_3\text{COCH}_3$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{CH}_3\text{CHO}$ ,  $\text{CH}_3\text{Cl}$ ).



# 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.



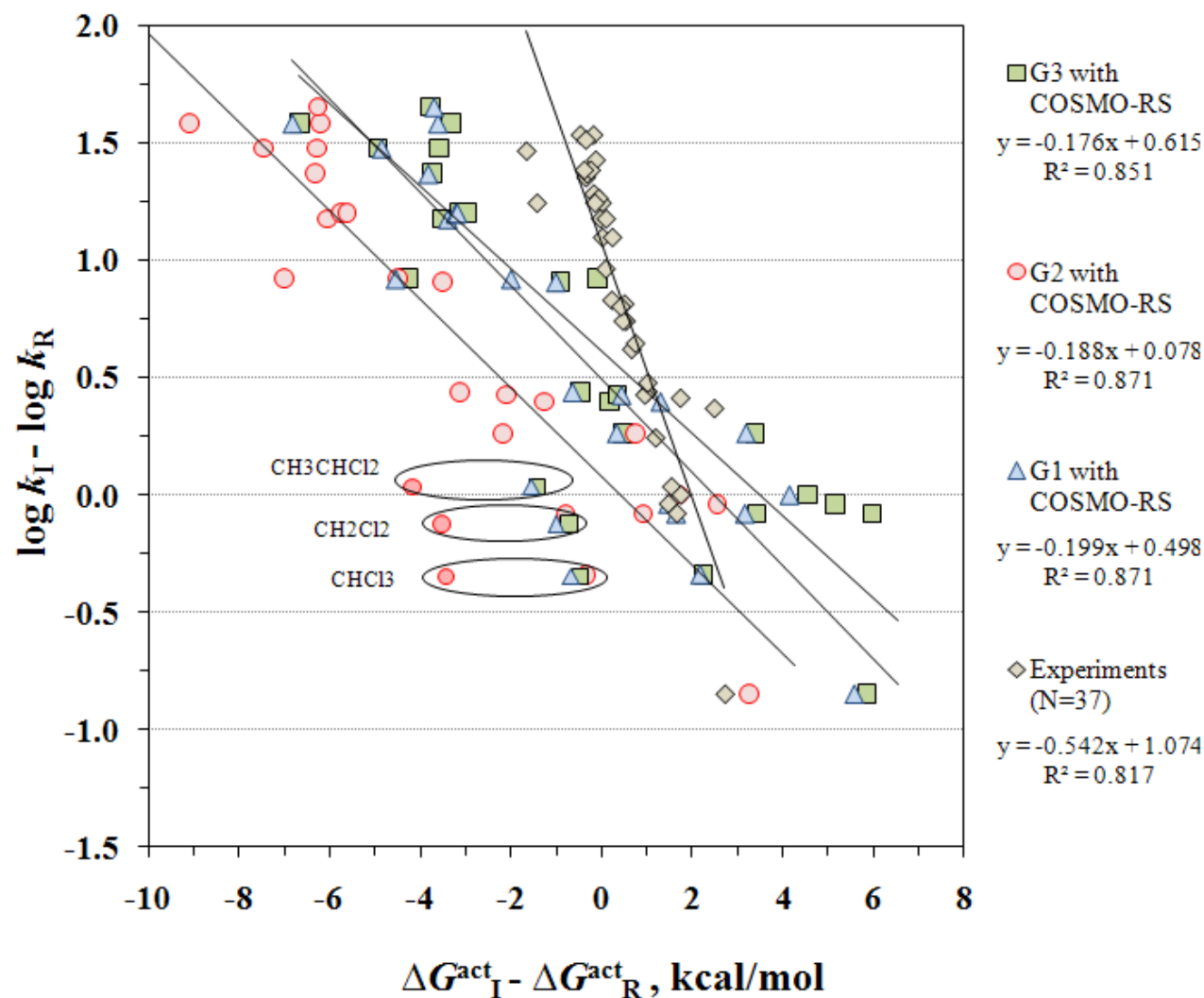
## Approaches: LFERs

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

- 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  $\Delta G_{\text{gas}}^{\ddagger}$  was chosen to establish the LFERs.



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



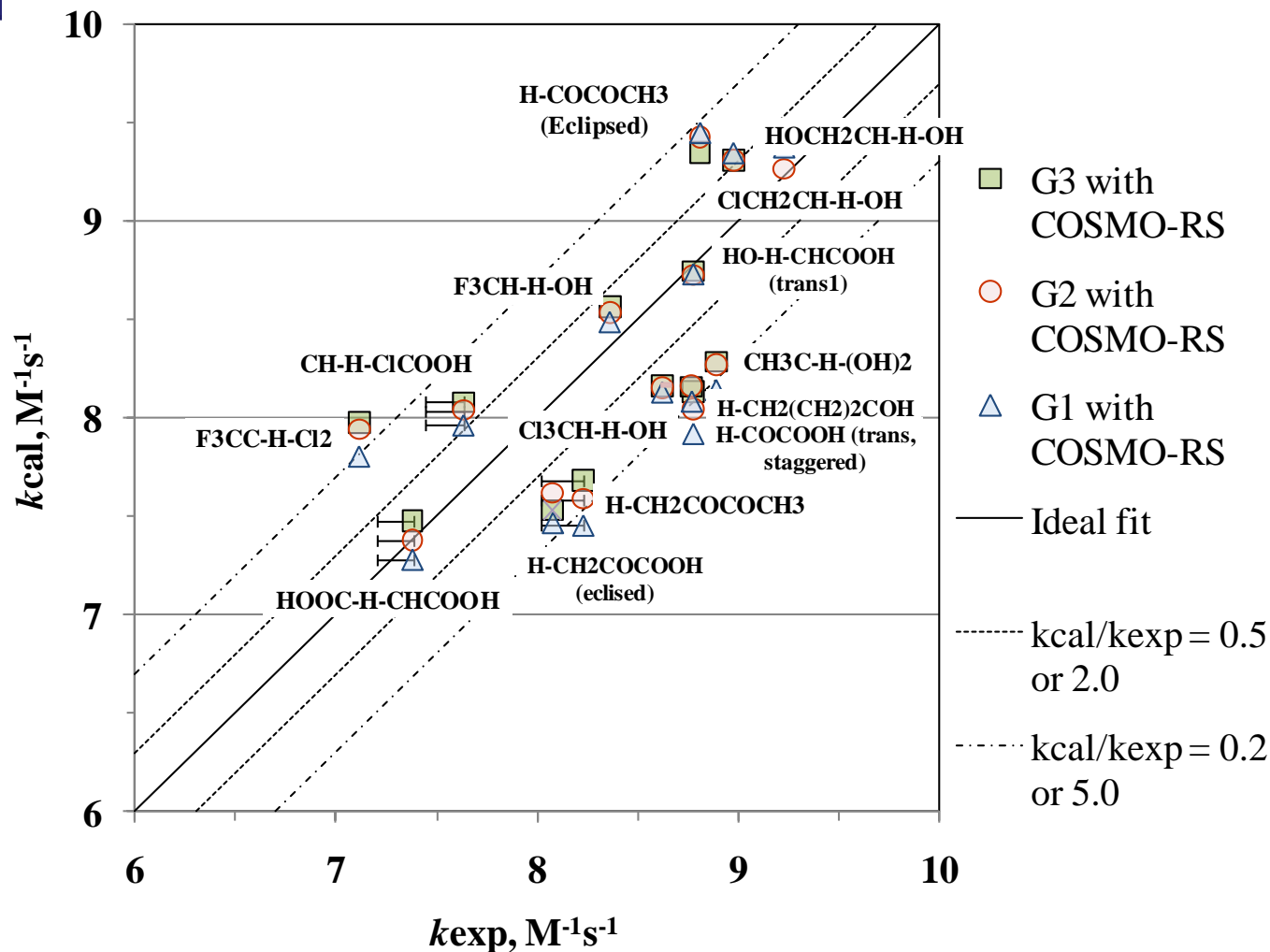
➤ 24 neutral compounds with single functional group

➤ Reaction of HO• with CH<sub>4</sub> is chosen as a reference reaction

➤ Calculated  $\Delta G_{\text{rxn, aq}}^{\text{act}}$  is approximately  $\pm 4$  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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