

Linear Free Energy Relationships for the Aqueous Phase Hydroxyl Radical Reactions with Ionized Species: Experimental and Theoretical Studies

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Outline

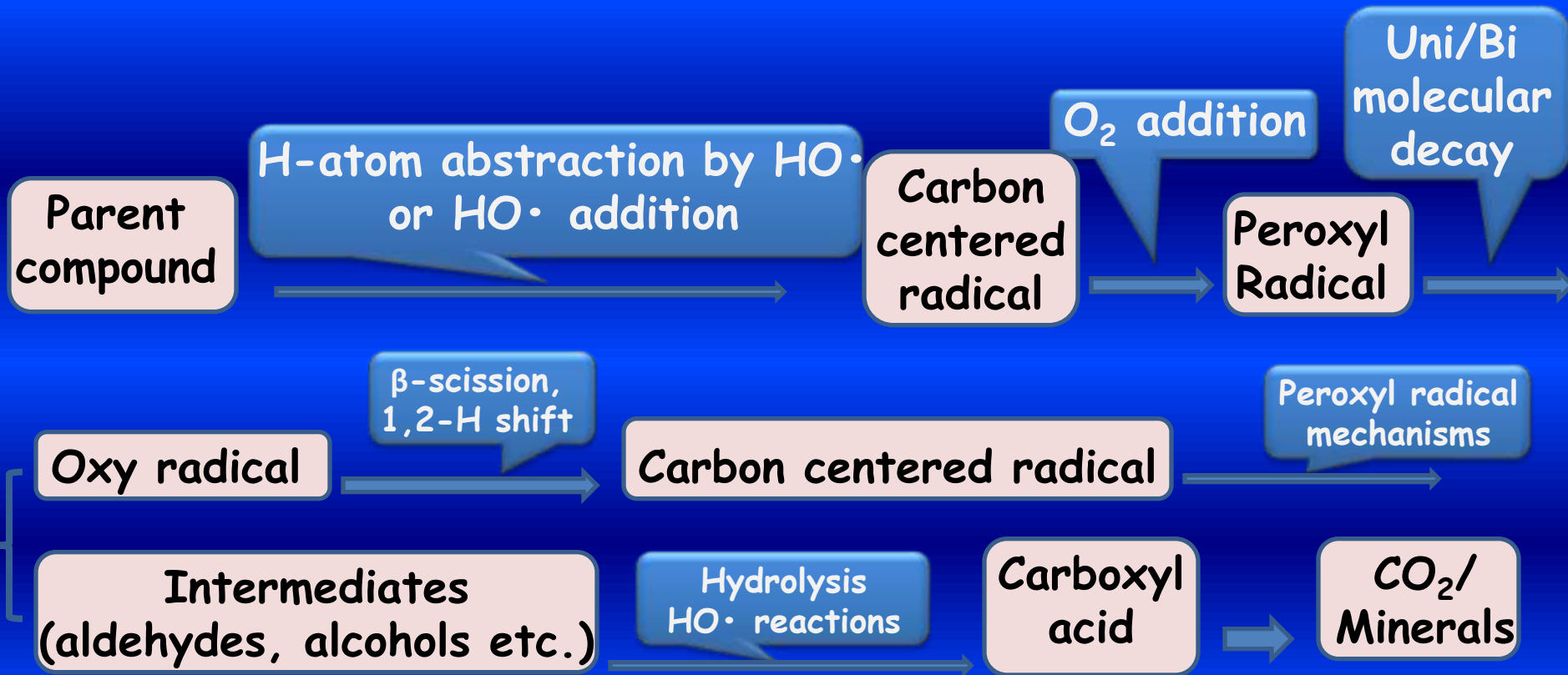
- Introduction to Advanced Oxidation Processes
- Our AOP project
- Background and Objective
- Linear Free Energy Relationships
- Results and Discussions: Experimental and Theoretical
- Acknowledgement

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

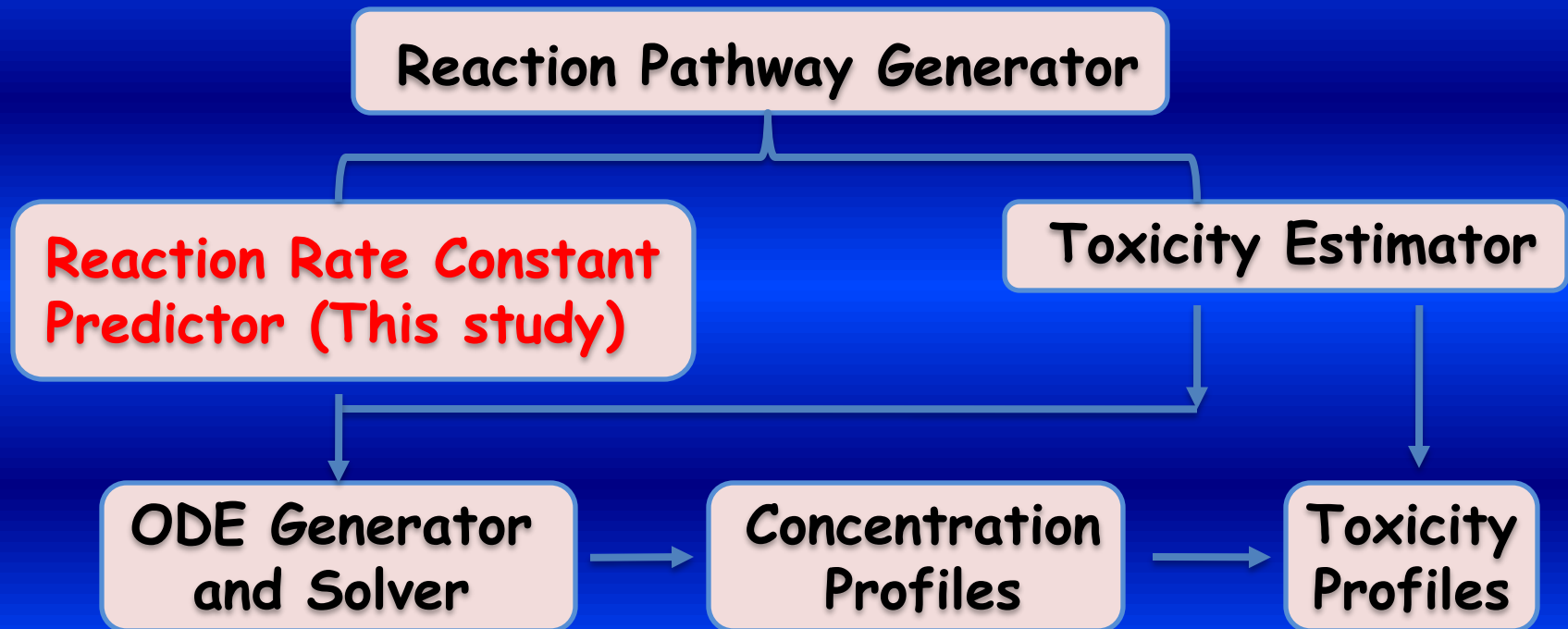
- ❖ Past experimental studies to reveal reaction mechanisms



- ❖ 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**

Introduction - AOP project -

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



Background

- ❖ Group Contribution Method to predict k_{HO} .
- ❖ Linear Free Energy Relationships (LFERs) for neutral compounds
- ❖ Deprotonated acids
 - ❖ Haloacetate ions
 - ✓ Potential carcinogen and lower reactivity with HO•
 - ❖ Experimental studies
 - ✓ Only a few experimental investigations
 - ❖ Molecular modeling for ionized compounds
 - ✓ Magnitudes of solvation free energy are much larger than those for neutral compounds due to **large electrostatic contributions** resulting from the charge distribution at transition states

Objective

To establish LFERs for ionized compounds based on both experimental and theoretical studies

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

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

$\Delta G_{\text{rxn,aq}}^{\ddagger}$ is defined as a quasithermodynamic molar free energy of activation, kcal/mol.

$$\Delta G_{\text{extra}} = -RT \ln \gamma(T)$$

$\gamma(T)$ is a transmission coefficient that represents the effect of tunneling at temperature T

Linear Free Energy Relationships (Continued)

$$\Delta G_{\text{rxn, aq}}^{\ddagger} = G_{\text{aq}}^{\ddagger} - G_{\text{reactants, aq}}$$

G_{aq}^{\ddagger} is a quasithermodynamic quantity, kcal/mol, that indicates the free energy of the transition state

$G_{\text{reactants, aq}}$ is the molar free energy of reactants, kcal/mol

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

where

$$\Delta\Delta G_{\text{rxn, solvation}}^{\ddagger} = \left(G_{\text{solvation}}^{\ddagger} - G_{\text{solvation}}^{\ddagger, 0} \right) - \left(G_{\text{reactants, solvation}} - G_{\text{reactants, solvation}}^0 \right)$$

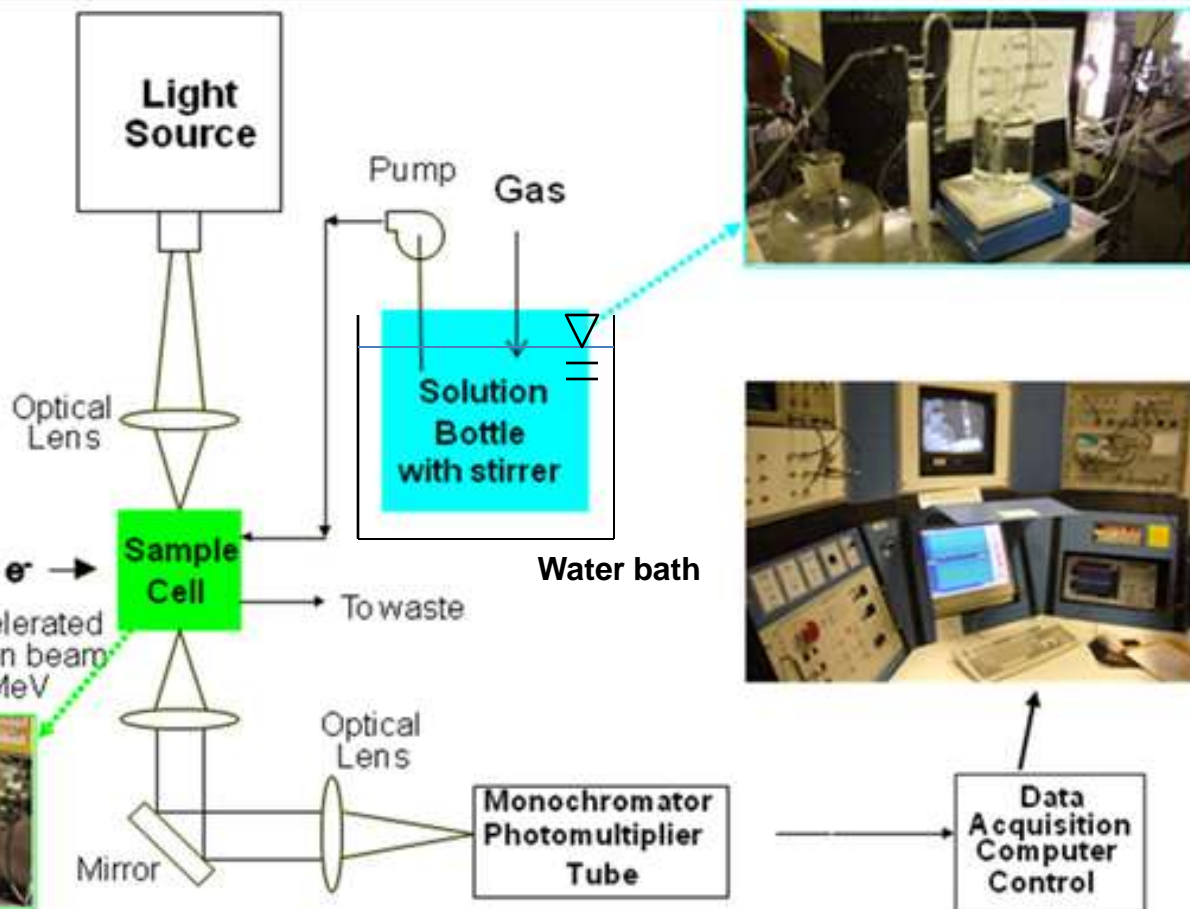
$\Delta\Delta G_{\text{rxn, solvation}}^{\ddagger}$ is free energy of solvation, kcal/mol, for a reaction measured with respect to a system composed of the pure, unperturbed aqueous phase at equilibrium and the solute molecule(s) in a separate phase considered to be an ideal gas;

$G_{\text{solvation}}^{\ddagger, 0}$ and $G_{\text{reactants, solvation}}^0$ are the standard state free energies of solvation for the transition state and reactants, respectively,

$G_{\text{solvation}}^{\ddagger}$ and $G_{\text{reactants, solvation}}$ are the free energies of solvation that are computed in solution for the transition state and reactants, respectively

Experimental: Approach and procedure 1

- Electron-pulse radiolysis coupled with standard time-resolved detection method



Injected Electron Beam (130 kV)

e^-

Acceleration section

RF Accelerated Electron beam 8MeV

Light Source

Optical Lens

Pump

Gas

Solution Bottle with stirrer

Water bath

Sample Cell

To waste

Optical Lens

Mirror

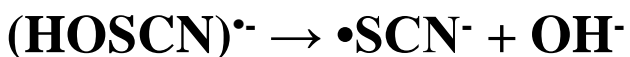
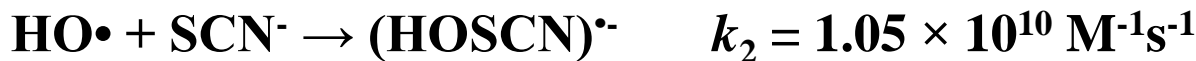
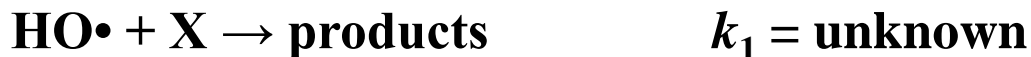
Monochromator Photomultiplier Tube

Data Acquisition Computer Control



Experimental: Approach and procedure 2

➤ Competition kinetics with use of thiocyanate ion (SCN^-)

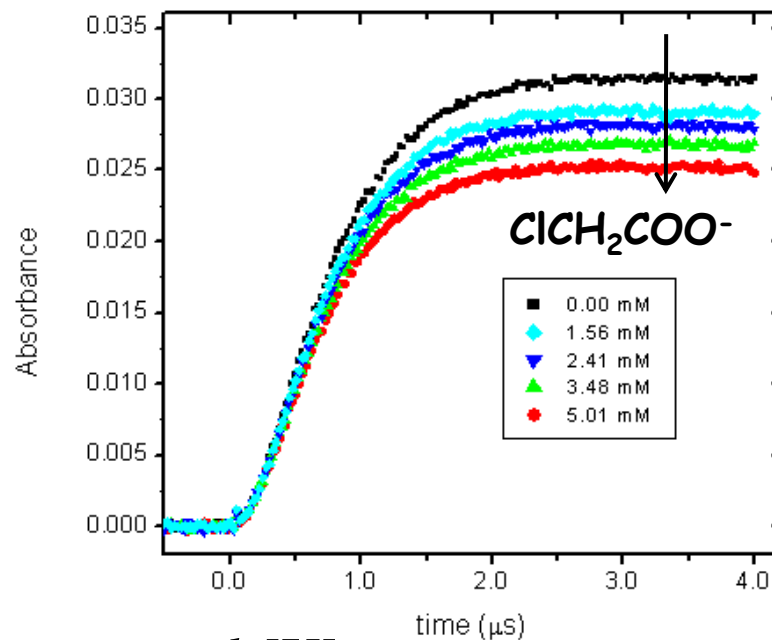


➤ Absorbance of $(\text{SCN})_2\cdot^-$ is measured as a function of time at wavelength of 472 nm.

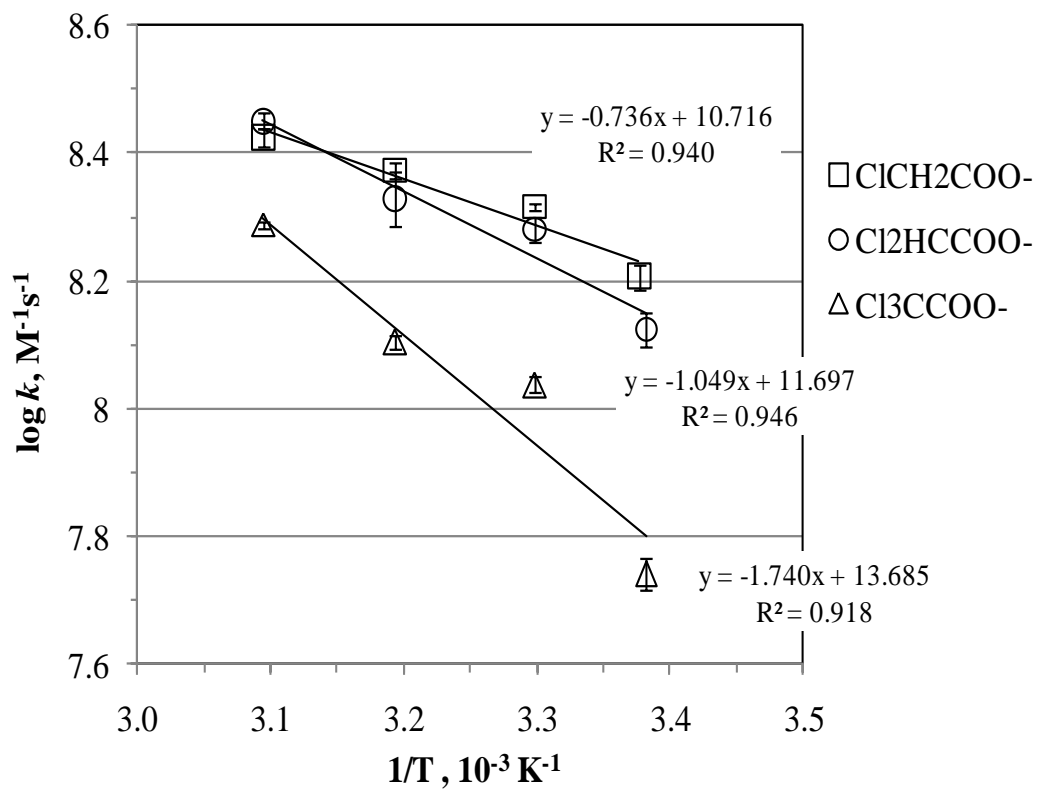
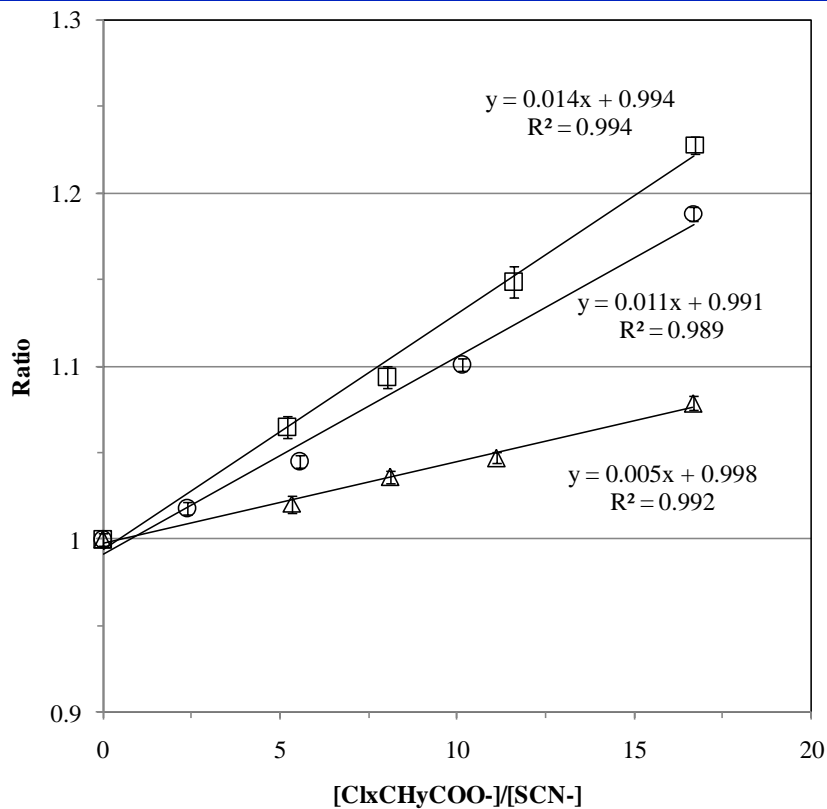
$$\begin{aligned} [\text{HO}\cdot + \text{SCN}^-] : [\text{HO}\cdot + \text{X}] \\ &= k_2 [\text{SCN}^-] : k_1 [\text{X}] \\ &= A_{[\text{SCN}^-]+[\text{X}]} : (A_{[\text{SCN}^-]} - A_{[\text{SCN}^-]+[\text{X}]}) \end{aligned}$$

$$\frac{1}{A_{[\text{SCN}^-]+[\text{X}]}} = \frac{1}{A_{[\text{SCN}^-]}} + \frac{k_1[\text{X}]}{A_{[\text{SCN}^-]}k_2[\text{SCN}^-]} \Leftrightarrow \frac{A_{[\text{SCN}^-]}}{A_{[\text{SCN}^-]+[\text{X}]}} = 1 + \frac{k_1[\text{X}]}{k_2[\text{SCN}^-]}$$

$$\frac{[(\text{SCN})_2\cdot^-]_0}{[(\text{SCN})_2\cdot^-]} = 1 + \frac{k_1[\text{X}]}{k_2[\text{SCN}^-]}$$



Results and Discussion: Experimental



$$\frac{[(SCN)_2]_0}{[(SCN)_2]} = 1 + \frac{k_1[X]}{k_2[SCN^-]}$$

- ✓ Arrhenius plot: $\log k$ versus $1/T$
- ✓ slope = $-E_a/2.3R$
- ✓ y-axis = $\log A$

$$E_a = \Delta H_{rxn}^{act} + RT$$

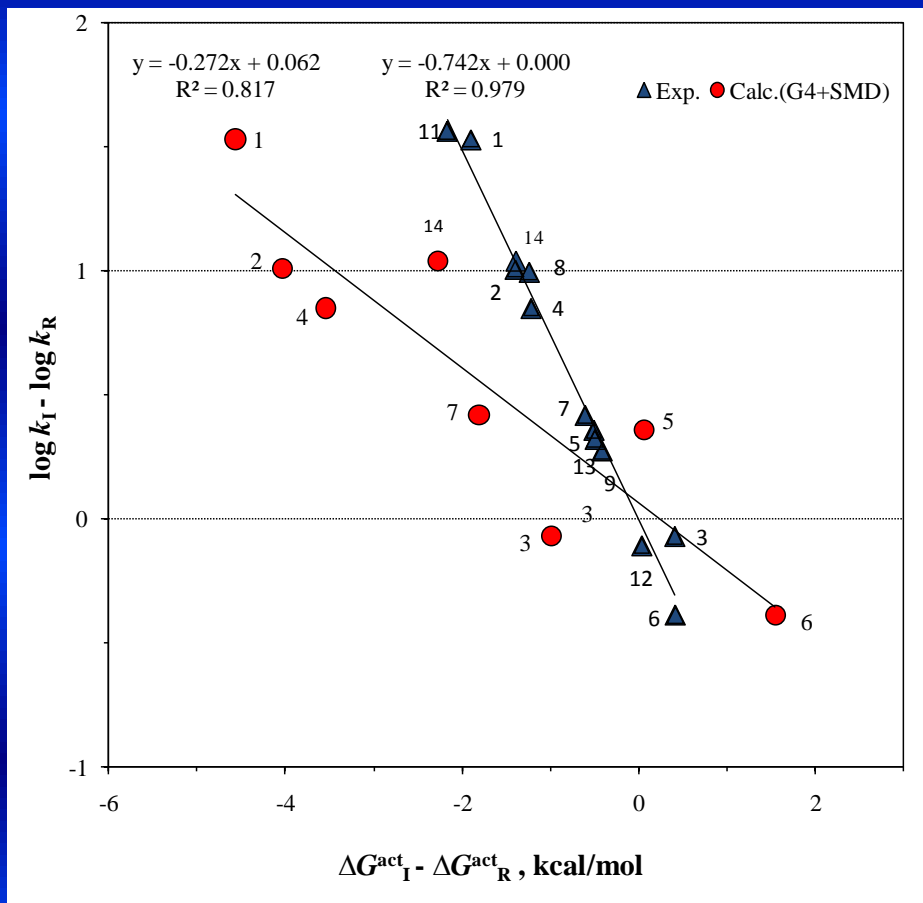
$$A = \frac{ekT}{h} \exp\left(\frac{-\Delta S_{rxn}^{act}}{R}\right)$$

$$\Delta G_{rxn}^{act} = \Delta H_{rxn}^{act} - T\Delta S_{rxn}^{act}$$

Theoretical: Approach

- ✓ $G1, G2$ and $G3$ with COSMO-RS significantly overestimates the aqueous phase free energy of activation due to the large electrostatics resulting from ionized compounds.
- ✓ $G4$ with the SMD solvation model (Marenich et al., 2009)
- ✓ $G4$ performs equivalent to CCSD(T) and QCISD(T) with significantly less computational cost but similar accuracy.
- ✓ SMD includes:
 - 1) **nonelectrostatic interactions** (cavity formation, free energy of repulsion and dispersion)
 - 2) **long range solute-solvent interaction in bulk phase**
 - 3) calculates electrostatic interaction based on the charge density of the solute (Marenich et al., 2009)
- ✓ Change of state from gaseous phase of 1 atm to aqueous phase concentration of 1 M (i.e., 1.89 kcal/mol) is included.
- ✓ **Solvent cage effects** (2.96 kcal/mol of reduction) based on the free volume theory.

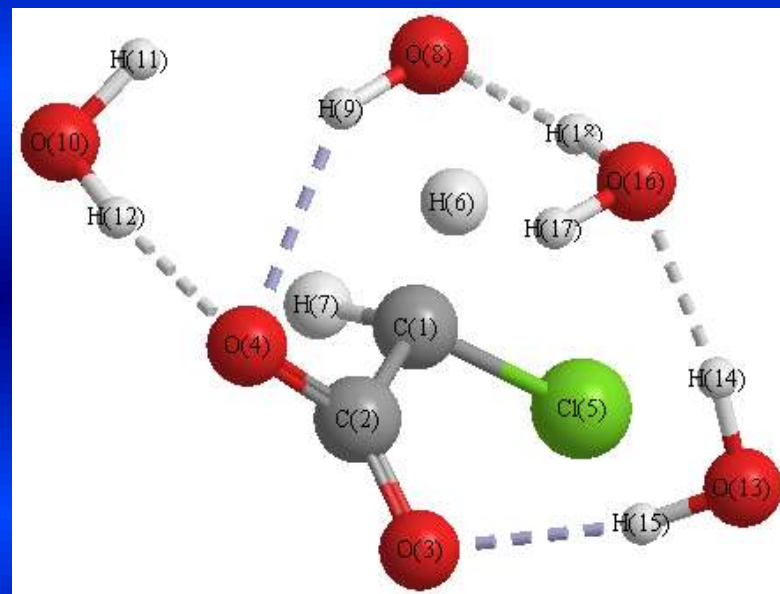
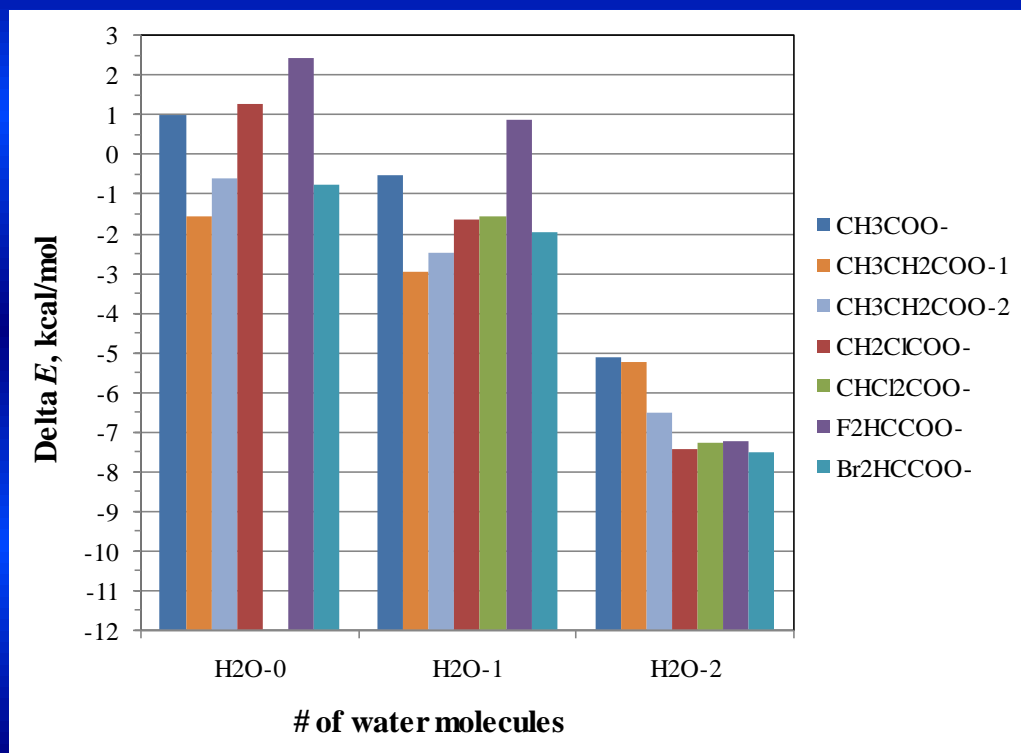
Results and Discussion: LFERs for ionized compounds



- 1: Formate; 2: Propionate;
 - 3: Malonate; 4: Succinate;
 - 5: Chloroacetate;
 - 6: Difluoroacetate;
 - 7: Dibromoacetate;
 - 8: Pyruvate; 9: Dichloroacetate;
 - 10: Acetate; 11: Glyoxylate;
 - 12: Trichloroacetate;
 - 13: Tribromoacetate;
 - 14: Lactate
- \diamond Reaction of $\text{HO}\cdot$ with acetate ion is used as a reference reaction

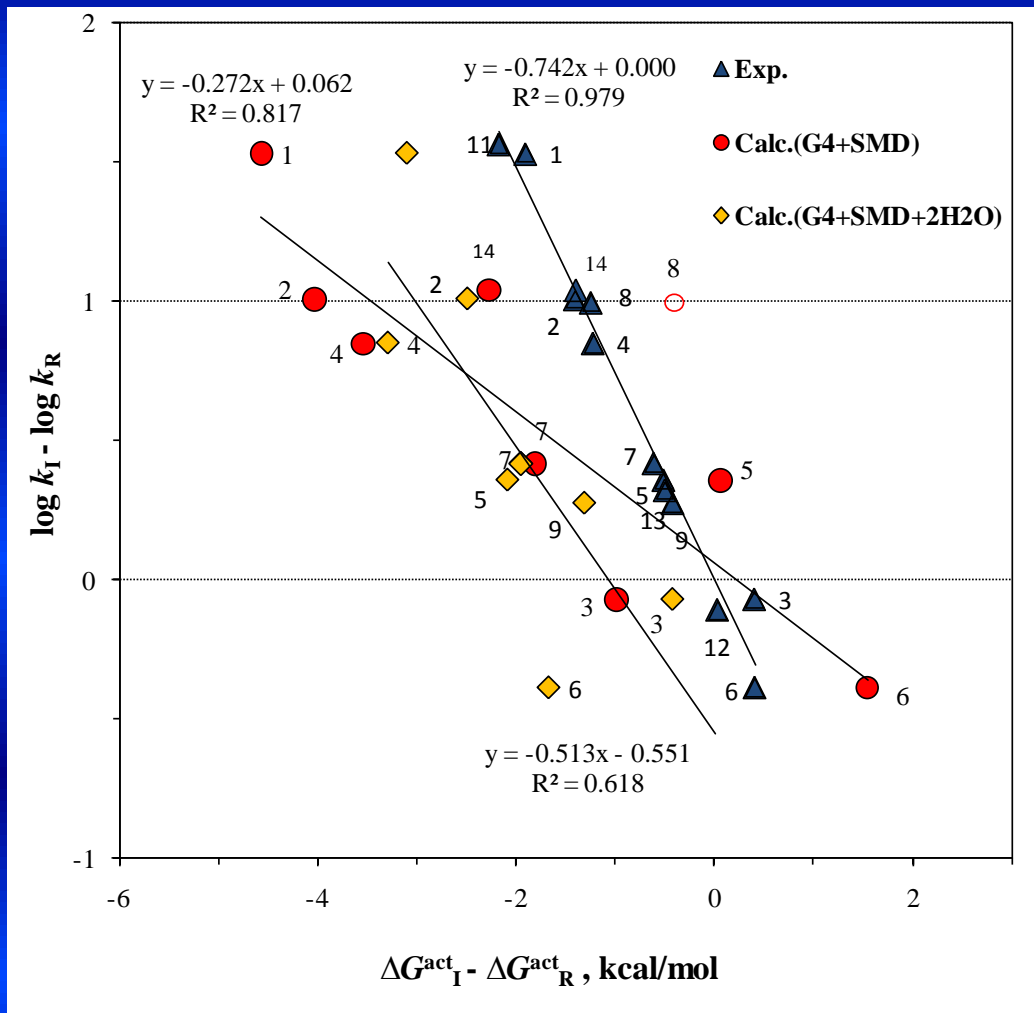
- A linear relation is observed for 10 carboxylates.
- 8 data were within ± 2 kcal/mol from the experimental values except formate (2.23 kcal/mol) and propionate (2.19 kcal/mol)
- Sample deviation (SD) for 10 compounds is 0.27
- Considering rate constant expression based on TST, 1 kcal/mol of difference in $\Delta G_{\text{rxn, aq}}^\ddagger$ causes 5.4 times difference in rate constant¹³

Results and Discussion: Addition of Explicit Water Molecules



- Water molecule is able to stabilize the developing negative charge on $\text{HO}\cdot$ and COO^- at the transition state by acting as a hydrogen bond donor.
- An addition of explicit water molecules to the SMD model predicts the barrier height lower by including **explicit nonbulk electrostatic contribution** that represents the deviation of short-range electrostatics from bulk electrostatics.

Results and Discussion: Addition of Explicit Water Molecules



- 1: Formate; 2: Propionate;
- 3: Malonate; 4: Succinate;
- 5: Chloroacetate;
- 6: Difluoroacetate;
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- 12: Trichloroacetate;
- 13: Tribromoacetate;
- 14: Lactate

❖ Reaction of HO· with acetate is used as a reference reaction

- A linear correlation for LFER with an addition of explicit water molecules is observed.
- An addition of explicit water molecules to the SMD model makes the LFER closer to that is obtained from the experiments

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End