# Forecasting the Environmental Impacts of New Energetic Materials

## Paul G. Tratnyek

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*http://cgr.ebs.ogi.edu/iron/*

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## Principles of Green Chemistry

1. **Prevention**: It is better to prevent waste ...
2. **Atom Economy**: Maximize the incorporation of all materials ...
3. **Less Hazardous Chemical Syntheses**: Use and generate substances that possess *little or no toxicity to human health and the environment*.
4. **Designing Safer Chemicals**: Chemical products should be designed to effect their desired function while minimizing their toxicity.
5. **Safer Solvents and Auxiliaries**: Unnecessary or innocuous ...
6. **Design for Energy Efficiency**: Energy requirements minimized ...
7. **Use of Renewable Feedstocks**: Raw materials and feedstocks should be renewable ...
8. **Reduce Derivatives**: Derivatization should be minimized ...
9. **Catalysis**: Catalytic are superior to stoichiometric reagents ...
10. **Design for Degradation**: Chemical products should be designed so that they *break down into innocuous degradation products and do not persist in the environment*.
11. **Real-time analysis for Pollution Prevention**: Real-time, in-process monitoring and control ...
12. **Inherently Safer Chemistry for Accident Prevention**: Substances should minimize the potential for *chemical accidents, including releases, explosions, and fires*.

Anastas, P. T.; Warner, J. C. (1998)

| Report Documentation Page | | *Form Approved* *OMB No. 0704-0188* |
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14. ABSTRACT
**The development of new energetic materials that are environmentally benign (i.e., ?green?) presumes an ability to predict the environmental fate and effects of candidate chemicals. Predicting the environmental impacts of chemicals is a long-standing challenge that has several parts, including the prediction of chemical properties (e.g., with quantitative structure-activity relationships [QSARs]) and the use of these properties to predict the chemical?s fate with multimedia assessment models. SERDP has recently funded three new projects with the overall goal of improving on the available tools for predicting the fate and effects of new energetic compounds. The three projects focus on (1) physico-chemical properties that determine partitioning and ultimately bioaccumulation, (2) reactivity properties that control the pathways and rates of compound transformation into products, and (3) the integration of both the above with transport to describe overall fate. These projects are particularly challenging because safety, regulatory, and security considerations make it impractical to do the experiments necessary to calibrate and validate empirical models for chemical property prediction. This will require a high degree of reliance on model compounds and on calculation of properties entirely from chemical-structure theory (?in silico?). Details regarding the approach to be taken in these projects will be presented, and the prospects for more cost-effective and proactive forecasting of the environmental impacts of energetic materials will be discussed.**

15. SUBJECT TERMS

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# KEYNOTE ADDRESS
# FORECASTING THE ENVIRONMENTAL IMPACTS OF
# NEW ENERGETIC MATERIALS

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The development of new energetic materials that are environmentally benign (i.e., "green"), presumes an ability to predict the environmental fate and effects of candidate chemicals. Predicting the environmental impacts of chemicals is a long-standing challenge that has several parts, including the prediction of chemical properties (e.g., with quantitative structure-activity relationships [QSARs]) and the use of these properties to predict the chemical's fate with multimedia assessment models.

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These projects are particularly challenging because safety, regulatory, and security considerations make it impractical to do the experiments necessary to calibrate and validate empirical models for chemical property prediction. This will require a high degree of reliance on model compounds and on calculation of properties entirely from chemical-structure theory ("in silico").
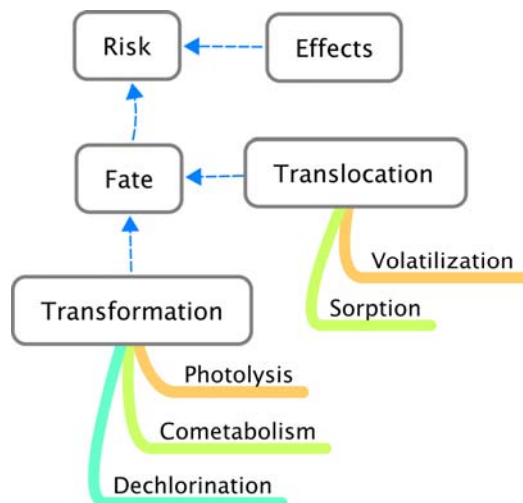
Details regarding the approach to be taken in these projects will be presented, and the prospects for more cost-effective and proactive forecasting of the environmental impacts of energetic materials will be discussed.

## FY2010 SERDP Statement of Need

**Predictive Techniques For Assessment of the Environmental Impact of New Munition Compounds**
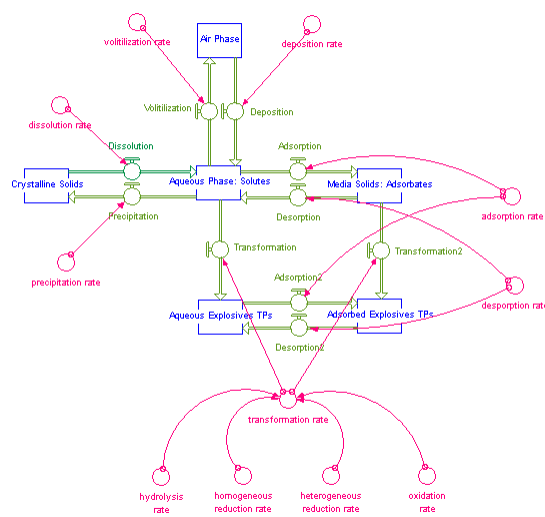
- Provide cost savings and risk reduction through avoidance of the development of munition compounds that may pose substantial environmental risk.

- Enable comprehensive environmental risk assessment for new munition compounds prior to full-scale production.

- Develop methods to utilize advanced, predictive techniques to improve the assessment of the environmental fate and transport of new, military-unique munition compounds.

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## Conceptual Model for Environmental Fate



- Risk =
  - *Effects (toxicity)*
  - *Fate*

- Fate =
  - *Translocation (transport)*
  - *Transformation (reaction)*

- Transformation =
  - *Degradation*
  - *Condensation*

## Elements of an Environmental Fate Model



- Fate Modeling and Simulation

  **Eric Weber**
  *US EPA, Athens, GA*

- Transport Property Prediction

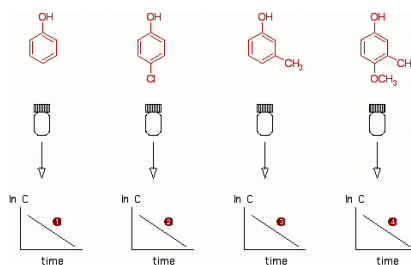  **Dominic Di Toro**
  *U. Delaware*

- Reaction Property Prediction

  **Paul Tratnyek**
  *Oregon Health & Science University*
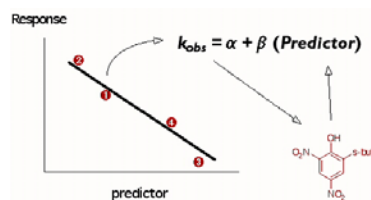
Stella® (http://www.iseesystems.com)

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## Obtaining Fate Property Data

1. Measure (in the lab) or look up "critical" values.
2. Estimated from calibrated empirical correlation models.
       (i.e., quantitative structure-activity relationships, QSARs)
3. Calculate directly from theory (i.e., ab initio quantum mechanics).
4. Estimate from fully in silico calibrated empirical correlation models.
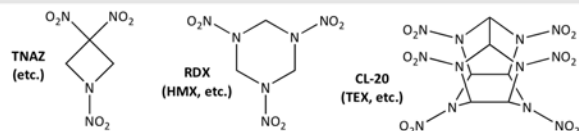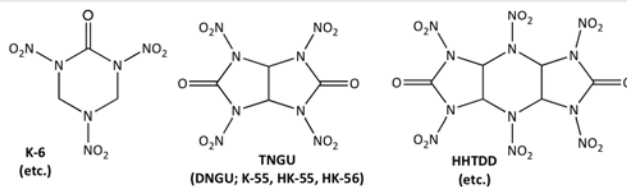


Standard Approach to QSAR Development

$k_{obs} = \alpha + \beta \, (Predictor)$

Tratnyek (1998, 2003)

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Representative and New Munition Compounds
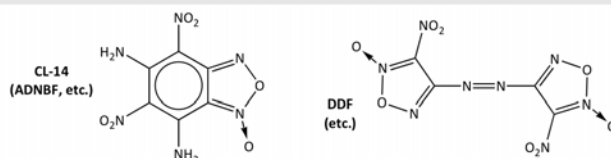
1. Fate Modeling and Simulation

**Development of an Environmental Fate Simulator for
New and Proposed Military-Unique Munitions Compounds**

**Eric Weber, Caroline Stevens,
Said Hilal, Gene Whelan, Rajbir Parmar**
*U.S. Environmental Protection Agency, Athens, GA*
Contaminant Fate/Transport, Modeling Software
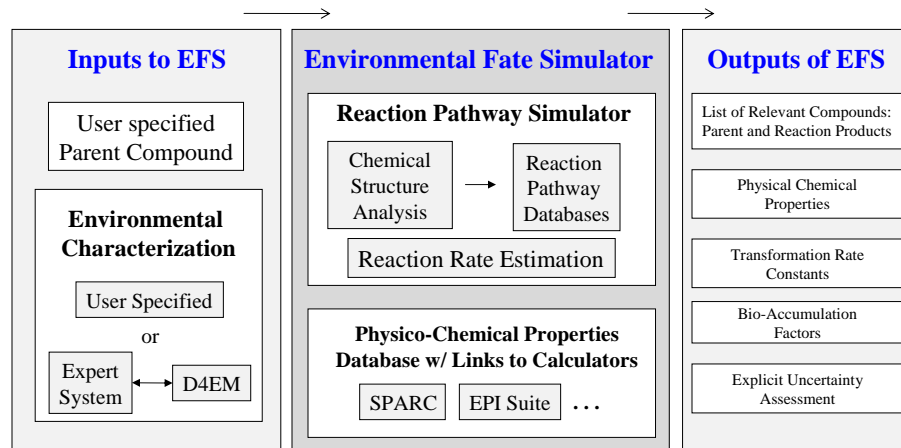
**Mitch Pelton**
*Pacific Northwest National Laboratory*
Software Engineering

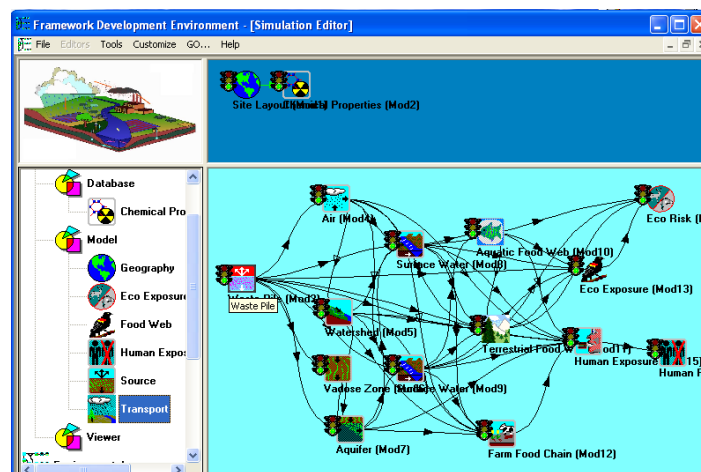**Jeff Gerald**
*U.S. Army Corps of Engineers*
Software Engineering

# 1. Fate Modeling and Simulation

| **Inputs to EFS** | **Environmental Fate Simulator** | **Outputs of EFS** |
|---|---|---|

**Inputs to EFS**

User specified Parent Compound

**Environmental Characterization**

User Specified

or

Expert System → D4EM

**Environmental Fate Simulator**

**Reaction Pathway Simulator**

Chemical Structure Analysis → Reaction Pathway Databases

Reaction Rate Estimation

**Physico-Chemical Properties Database w/ Links to Calculators**

SPARC | EPI Suite | . . .

**Outputs of EFS**

List of Relevant Compounds: Parent and Reaction Products

Physical Chemical Properties

Transformation Rate Constants

Bio-Accumulation Factors

Explicit Uncertainty Assessment

*Data for Environmental Modeling

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# 1. Fate Modeling and Simulation

## FRAMES: Framework for Risk Analysis in Multi-Media Environmental Systems

## 1. Fate Modeling and Simulation

### Sparc Performs Automated Reasoning in Chemistry



http://sparc.chem.uga.edu/sparc/

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## 2. Translocation Properties and Prediction

**Developing Quantum Chemical and Polyparameter
Models for Predicting Environmentally Significant
Parameters for New Munition Compounds**

**Dominic M. Di Toro, Herbert Allen, Stanley Sandler**
*University of Delaware*
Chemical Fate/Effects, Chemical Modeling

**Ronald Checkai, Roman Kuperman, Michael Simini**
*U.S. Army Edgewood Chemical Biological Center*
Fate and Effects of Explosive*s*

**Geoffrey Sunahara**
*CNRC, Biotechnology Research Institute Analytical Chemistry*
Analytical Chemistry, Toxicology

## 2. Transport Properties and Prediction

- Aqueous Solubility
  - $S_W$
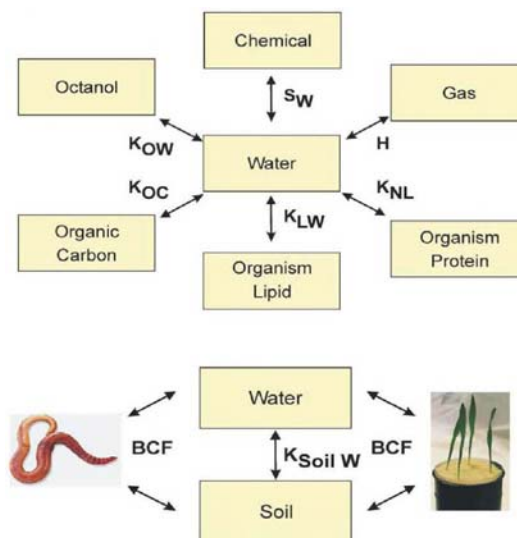- Partition Coefficients
  - $K_{OW}, K_{OC}, K_{LW}, K_{NL}$
- Henry's Law Const
  - H, HLC
- Bioconcentration
  - BCF
- *Metabolism*

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## 2. Transport Properties and Prediction

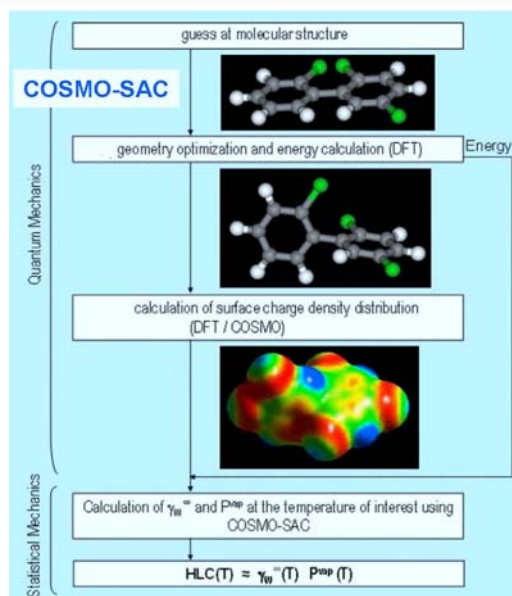- Calibrated Empirical Correlation Methods
  - LSERs
  - Polyparameter Models

- Models from Chemical Structure Theory
  - SPARC
  - Mixed QM

**Fully In Silico Calibration of
Empirical Predictive Models for Environmental Fate
Properties of Novel Munitions Compounds**

**Paul G. Tratnyek**
*Oregon Health & Science University*
Environmental fate and remediation of organic contaminants;
Structure-property relationships for contaminant fate properties

**Eric J. Bylaska, Kurt R. Glaesemann**
*Pacific Northwest National Laboratory*
Development and application of theoretical models for
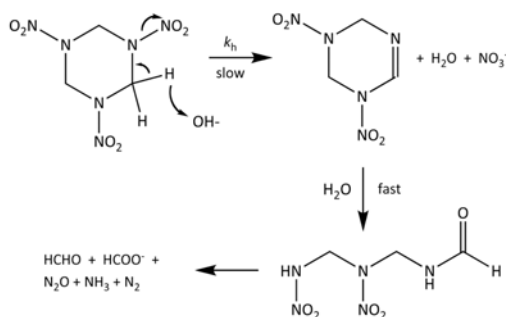chemical reactions; High-performance computing

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- *Overall Goal*: **Develop quantitative models** that can predict the reactivity (i.e., transformation) of future explosive compounds by the four major reaction pathways:
  - Objective 1: Hydrolysis/Elimination
  - Objective 2: Homogeneous nitro reduction (in solution)
  - Objective 3: Heterogeneous nitro reduction (on surfaces)
  - Objective 4: Oxidative coupling of nitro reduction products
- *Supporting Goal*: **Demonstrate a novel strategy** for fully in silico calibration of predictive models for properties of chemicals:
  - End product will be quantitative structure-activity relationships (QSARs) because they are the most accessible to non specialists.
  - Use "in silico calibration" to overcome the practical restrictions on conventional methods of QSAR development that rely on calibration with experimental data.
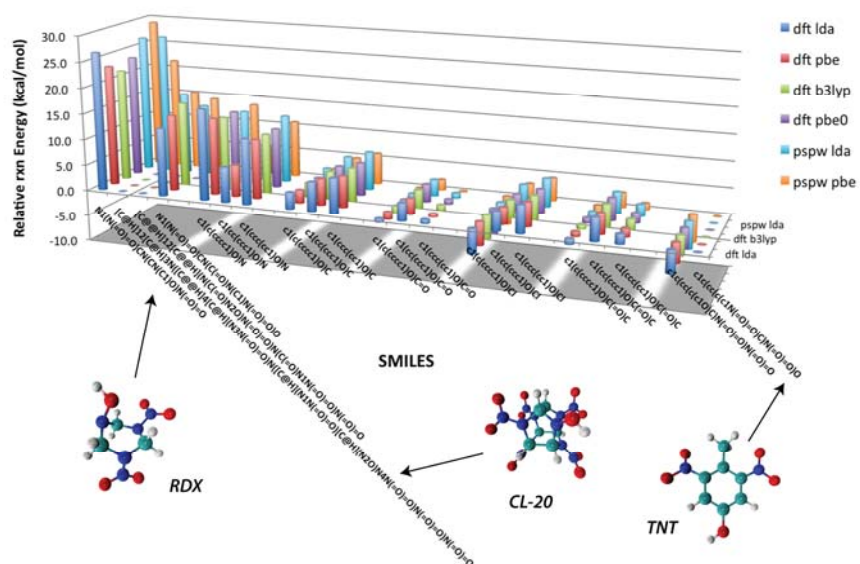
# 3. Reaction Properties and Prediction

**Hydrolysis/Elimination (Objective 1)**

▪Degradation by water is the ubiquitous environmental pathway.

▪Also the basis for some remediation strategies.

▪Mechanism well known for the common explosives (TNT, RDX).

▪Rates of hydrolysis for explosives vary from very fast to very slow.

▪Simplest, test case.



Mechanism for hydrolysis of a prototypical nitramine explosive (RDX).

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# 3. Reaction Properties and Prediction

## Summary & Acknowledgements

### Prospects

- Designing new munition compounds for sustainability requires novel methods for predicting environmental fate (and effects and risk).

- Fate determining processes that must be considered including partitioning, sorption, bioaccumulation, hydrolysis and reduction.

- Fate determining properties can be estimated from empirical correlations or chemical structure theory, with the latter rapidly becoming more available and accurate.

### People

- Eric Bylaska, Kurt Glaesemann, Ali Salter

- Eric Weber, Dominic Di Toro

**Pacific Northwest**
NATIONAL LABORATORY

### Funding

- SERDP

**SERDP**
DOD · EPA · DOE

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## Supporting Slides

## Forecasting the Environmental Impacts of New Energetic Materials

### Paul G. Tratnyek

*Eric Bylaska, Kurt Glaesemann (PNNL),*
*Dominic Di Toro (U. Delaware), and Eric Weber (USEPA)*

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*http://cgr.ebs.ogi.edu/iron/*

## QSARs for Nitro Reduction

**Examples QSARs for Nitro Reduction (Objectives 2 & 3)**

Table 3. Summary of quantitative structure–activity relationships for nitro reductions

| Equation | Reductant | Contaminant | Equation[a] | Statistics[b] | References |
|---|---|---|---|---|---|
| 7 | Aquifer column | Nitrobenzenes | $\log k_{rel} = 0.01(\pm 0.02)\cdot E^1/0.059 + 0.05(\pm 0.14)^*$ | 0.04 (10) | [9] |
| 8 | Aquifer column + acetate | Nitrobenzenes | $\log k_{rel} = 0.03(\pm 0.02)\cdot E^1/0.059 + 0.2(\pm 0.1)^*$ | 0.35 (9) | [9] |
| 9 | Ferrogenic column | NACs | $\log k_{rel} = 0.05(\pm 0.04)\cdot E^1/0.059 + 0.5(\pm 0.3)^*$ | 0.12 (15) | [10] |
| 10 | Inoculated column[e] | NACs | $\log k_{rel} = 0.01(\pm 0.01)\cdot E^1/0.059 + 0.06(\pm 0.07)^*$ | 0.10 (10) | [10] |
| 11 | $Fe^{2+}_{(ads)}/Fe_3O_{4(s)}$ | Nitrobenzenes $(m,p)$ | $\log k_{rel} = 0.35(\pm 0.03)\cdot E^1/0.059 + 2.7(\pm 0.3)^*$ | 0.95 (7) | [30] |
| 12 | $Fe^{2+}_{(ads)}/FeOOH_{(s)}$ | NACs | $\log k_{rel} = 0.53(\pm 0.04)\cdot E^1/0.059 + 4.0(\pm 0.3)^*$ | 0.98 (6) | [10] |
| 13 | $Fe^0$ | Nitrobenzenes | $\log k_{rel} = 0.10(\pm 0.01)\cdot E^1/0.059 + 0.79(\pm 0.05)^*$ | 1.00 (3) | [8] |
| 14 | $Fe^0$ | Nitrobenzenes | $\log Q = 0.27(\pm 0.03)\cdot E^1/0.059 + 2.0(\pm 0.02)^*$ | 0.97 (4) | [8] |
| 15 | $NOM/H_2S^d$ | NACs | $\log k = 1.0\cdot E^1/0.059 + 4.4^{**}$ | 0.91 (10) | [29] |
| 16 | $Jug/H_2S$ | (poly)NACs | $\log k = 1.25(\pm 0.03)\cdot E^1/0.059 + 9.2(\pm 0.2)$ | 1.00 (5) | [10] |
| 17 | $Jug/H_2S$ | Nitrobenzenes $(o,m,p)$ | $\log k = 0.99(\pm 0.06)\cdot E^1/0.059 + 7.2\ (\pm 0.5)^{*f}$ | 0.97 (10) | [28] |
| 18 | $Lawsone/H_2S$ | Nitrobenzenes $(o,m,p)$ | $\log k = 0.99\cdot E^1/0.059 + 8.47^{*f}$ | 0.97 (7) | [28] |
| 19 | FeP/Cys | Nitrobenzenes $(m,p)$ | $\log k = 0.60\cdot E^1/0.059 + 4.95^{*f}$ | 0.99 (7) | [28] |
| 20 | FeP/Cys | Nitrobenzenes $(o)$ | $\log k = 0.93\cdot E^1/0.059 + 8.65^{*f}$ | 0.99 (3) | [28] |
| 21 | FeP/Cys | Nitrobenzenes | $\log k_{rel} = 0.60(\pm 0.03)\cdot E^1/0.059 + 4.5(\pm 0.2)^*$ | 0.99 (7/3) | [9] |

Tratnyek, P. G., E. J. Weber, and R. P. Schwarzenbach. 2003. Quantitative structure-activity relationships for chemical reductions of organic contaminants. Environmental Toxicology and Chemistry 22(8): 1733-1742.

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## Computer Resources

**Hardware**:
- Chinook Super Computer:
  - 2323 nodes
    Dual quad-core AMD Opteron CPUs
  - 163 Teraflops peak performance
- Other (NW/ICE Cluster):
  - 192 Nodes
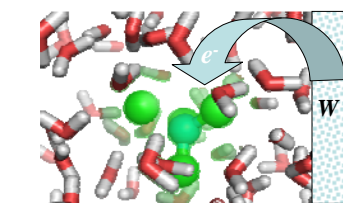    Intel Xeon quad-core CPUs
  - 14.3 TeraFlops of peak performance

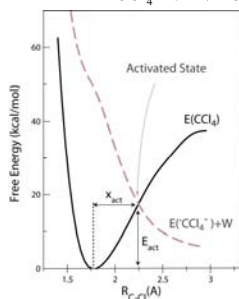**Software**:
- NWChem
- Other (Gaussian, GAMESS, etc.)

## Preliminary Data



$$CCl_4 + e^- \rightarrow CCl_3^\bullet + Cl^-$$

- Concerted electron transfer bond breaking mechanism
- Free energy calculation of dissociation profiles and redox potential using CCSD(T)/MM and DFT/MM descriptions
- CCSD(T) are in good agreement with experimental data for oxide-free iron cathodes

*Free Energy Activation Barriers at W = -1.2 V*

|  | CCSD(T)/MM | DFT/MM | Exp |
|---|---|---|---|
| $E_{act}$ | 8.1 kcal/mol | 4.3 kcal/mol | 8.0 kcal/mol |

Valiev, M.; **Bylaska**, E. J.; Dupuis, M.; **Tratnyek**, P. G., *J. Phys. Chem. A* 2008, *112*, 2713.

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## Supporting Information

**QSAR Formulation—Selection of Framework**

**QSAR Formulation—Selection of Descriptors**