

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)



Environmental and Biomolecular Systems

Oregon Health & Science University

<http://www.ebs.ogi.edu/tratnyek/>

<http://cgr.ebs.ogi.edu/iron/>

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.*

Report Documentation Page		Form Approved OMB No. 0704-0188
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.		
1. REPORT DATE NOV 2010	2. REPORT TYPE	3. DATES COVERED 00-00-2010 to 00-00-2010
4. TITLE AND SUBTITLE Forecasting the Environmental Impacts of New Energetic Materials		5a. CONTRACT NUMBER
		5b. GRANT NUMBER
		5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER	
	5e. TASK NUMBER	
	5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Oregon Health & Science University, 20000 NW Walker Road, Beaverton, OR, 97006		8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S)
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited		
13. SUPPLEMENTARY NOTES Presented at the 15th Annual Partners in Environmental Technology Technical Symposium & Workshop, 30 Nov ? 2 Dec 2010, Washington, DC. Sponsored by SERDP and ESTCP. U.S. Government or Federal Rights License		
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		

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 14	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

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

DR. PAUL G. TRATNYEK
Oregon Health & Science University
20000 NW Walker Road
Beaverton, OR 97006
(503) 748-1023
tratnyek@ebs.ogi.edu

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”).

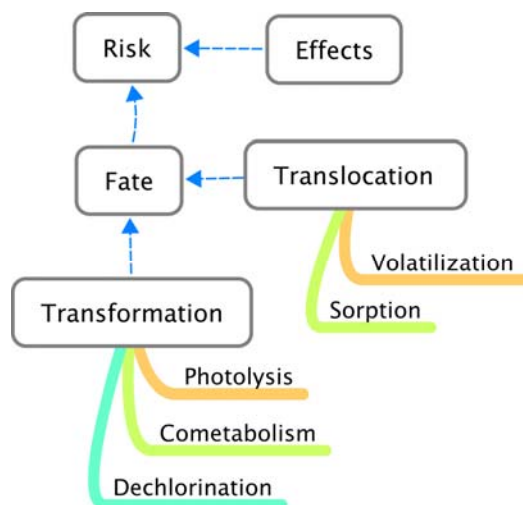
Details regarding the approach to be taken in these projects will be presented, and the prospects for more cost-effective and proactive forecasting of the environmental impacts of energetic materials will be discussed.



Predictive Techniques For Assessment of the Environmental Impact of New Munition Compounds

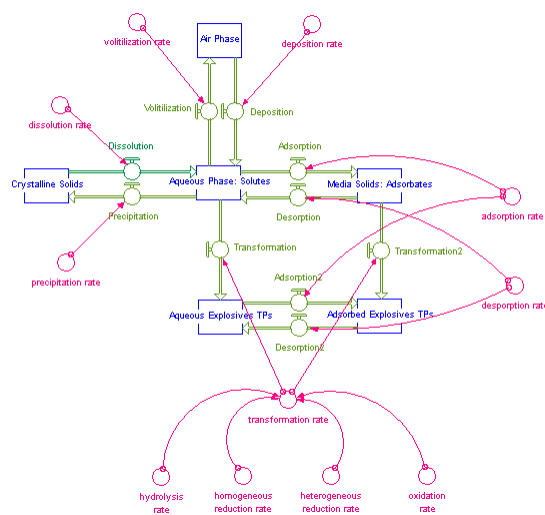
- Provide cost savings and risk reduction through avoidance of the development of munition compounds that may pose substantial environmental risk.
- Enable comprehensive environmental risk assessment for new munition compounds prior to full-scale production.
- Develop methods to utilize advanced, predictive techniques to improve the assessment of the environmental fate and transport of new, military-unique munition compounds.

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

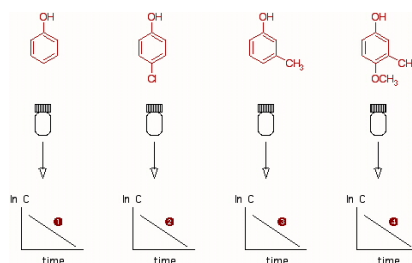
Paul Tratnyek
Oregon Health & Science University

Stella® (<http://www.iseesystems.com>)

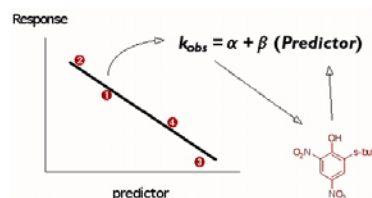
5

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

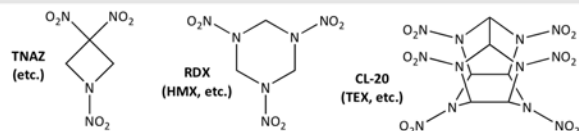


Tratnyek (1998, 2003)

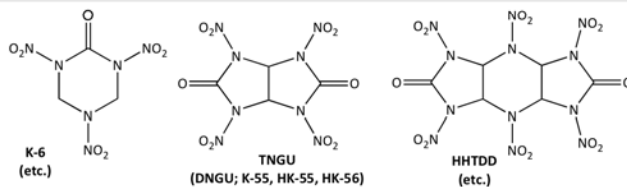
6

Representative and New Munition Compounds

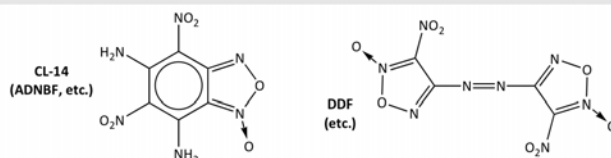
Nitramines



Nitroureas



Furoxans



7

1. Fate Modeling and Simulation

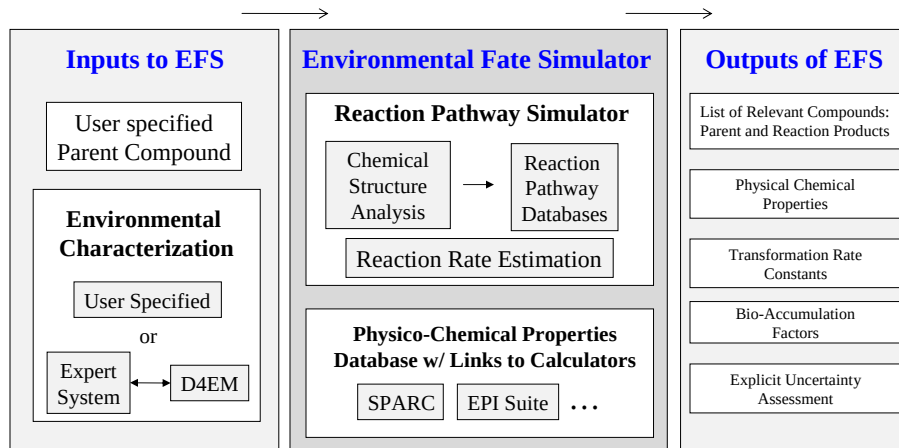
Development of an Environmental Fate Simulator for New and Proposed Military-Unique Munitions Compounds

**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



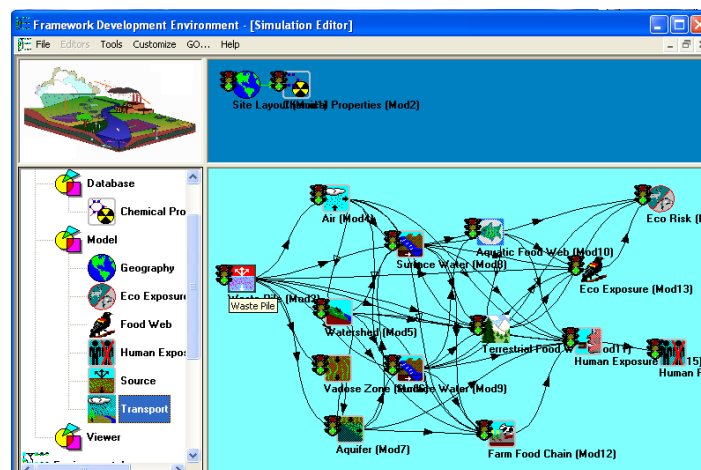
*Data for Environmental Modeling

Weber (ER-1736)

9

1. Fate Modeling and Simulation

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



Weber (ER-1736)

10

1. Fate Modeling and Simulation

Sparc Performs Automated Reasoning in Chemistry



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

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 Explosives

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}

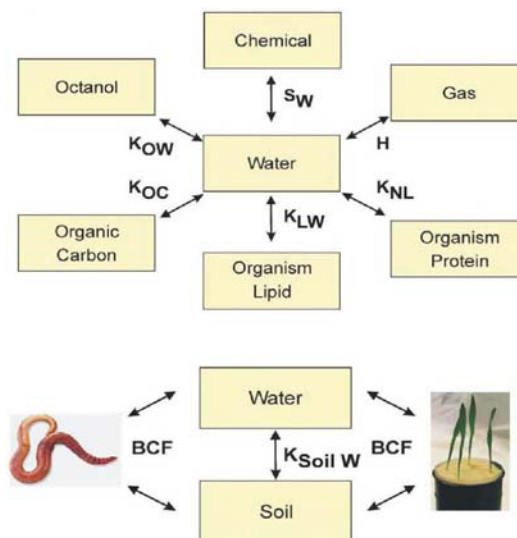
- Henry's Law Const

H , HLC

- Bioconcentration

BCF

- Metabolism



2. Transport Properties and Prediction

- Calibrated Empirical Correlation Methods

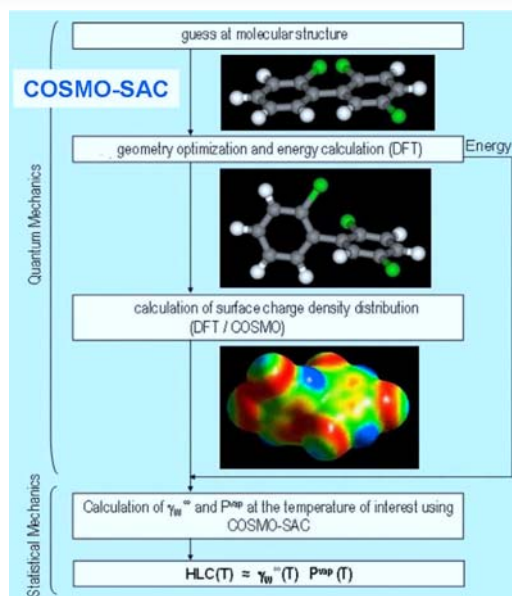
$LSERs$

$Polyparameter$
 $Models$

- Models from Chemical Structure Theory

$SPARC$

$Mixed QM$



3. Reaction Properties and Prediction

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

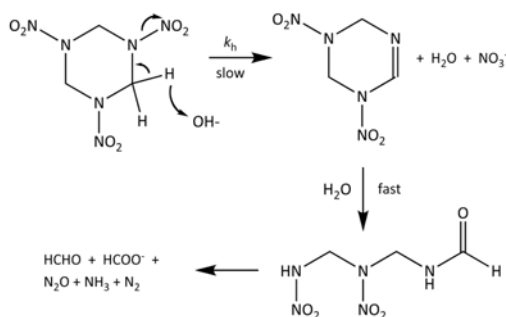
3. Reaction Properties and Prediction

- **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

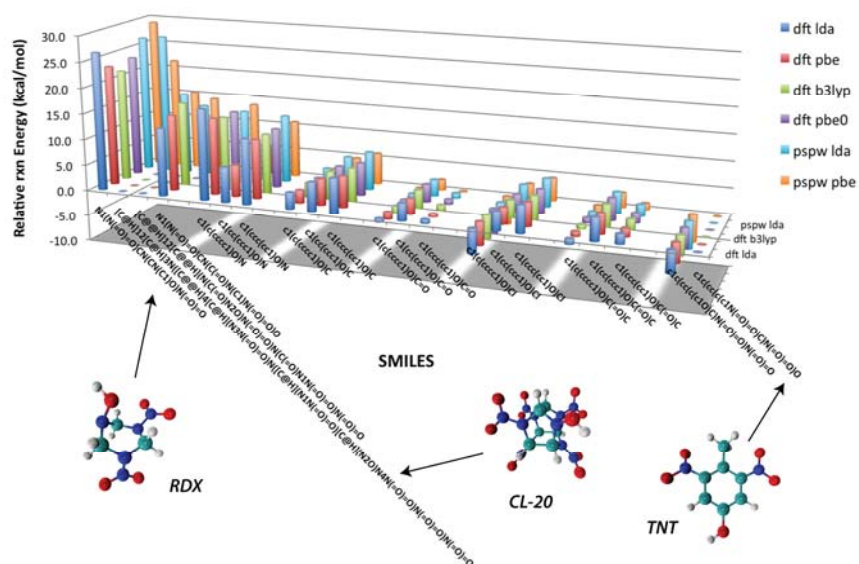
Hydrolysis/Elimination (Objective 1)

- 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).

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



Funding

- SERDP



19

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)



Environmental and Biomolecular Systems
Oregon Health & Science University
<http://www.ebs.ogi.edu/tratnyek/>
<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	$\log k_{\text{nt}} = 0.01(\pm 0.02) \cdot E^1/0.059 + 0.05(\pm 0.14)^*$	0.04 (10)	[9]
8	Aquifer column + acetate	Nitrobenzenes	$\log k_{\text{nt}} = 0.03(\pm 0.02) \cdot E^1/0.059 + 0.2(\pm 0.1)^*$	0.35 (9)	[9]
9	Ferrogenic column	NACs	$\log k_{\text{nt}} = 0.05(\pm 0.04) \cdot E^1/0.059 + 0.5(\pm 0.3)^*$	0.12 (15)	[10]
10	Inoculated column ^c	NACs	$\log k_{\text{nt}} = 0.01(\pm 0.01) \cdot E^1/0.059 + 0.06(\pm 0.07)^*$	0.10 (10)	[10]
11	$\text{Fe}^{2+}_{\text{aq}}/\text{Fe}_3\text{O}_4$	Nitrobenzenes (<i>m,p</i>)	$\log k_{\text{nt}} = 0.35(\pm 0.03) \cdot E^1/0.059 + 2.7(\pm 0.3)^*$	0.95 (7)	[30]
12	$\text{Fe}^{2+}_{\text{aq}}/\text{FeOOH}_{10}$	NACs	$\log k_{\text{nt}} = 0.53(\pm 0.04) \cdot E^1/0.059 + 4.0(\pm 0.3)^*$	0.98 (6)	[10]
13	Fe^0	Nitrobenzenes	$\log k_{\text{nt}} = 0.10(\pm 0.01) \cdot E^1/0.059 + 0.79(\pm 0.05)^*$	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 (<i>o,m,p</i>)	$\log k = 0.99(\pm 0.06) \cdot E^1/0.059 + 7.2 (\pm 0.5)^{**}$	0.97 (10)	[28]
18	Lawson/ H_2S	Nitrobenzenes (<i>o,m,p</i>)	$\log k = 0.99 \cdot E^1/0.059 + 8.47^{**}$	0.97 (7)	[28]
19	FeP/Cys	Nitrobenzenes (<i>m,p</i>)	$\log k = 0.60 \cdot E^1/0.059 + 4.95^{**}$	0.99 (7)	[28]
20	FeP/Cys	Nitrobenzenes (<i>o</i>)	$\log k = 0.93 \cdot E^1/0.059 + 8.65^{**}$	0.99 (3)	[28]
21	FeP/Cys	Nitrobenzenes	$\log k_{\text{nt}} = 0.60(\pm 0.03) \cdot E^1/0.059 + 4.5(\pm 0.2)^*$	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.

Tratnyek (2003)

21

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

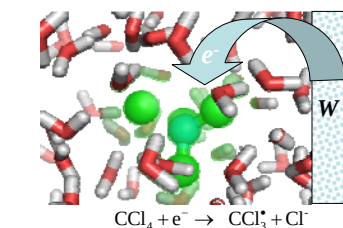
Software:

- NWChem
- Other (Gaussian, GAMESS, etc.)

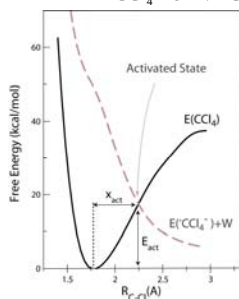


22

Preliminary Data



- 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 $W = -1.2 \text{ V}$

	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.

23

Supporting Information

QSAR Formulation—Selection of Framework

S \ E	O_2	OH	$^1\text{O}_2$	CrO_4^{2-}
$\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$				
$\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$				
$\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$				

24

Supporting Information

QSAR Formulation—Selection of Descriptors

