

# Reduction transformation of N-O Containing Compounds by Fe<sup>II</sup> Species

Yiling Chen and Huichun (Judy) Zhang\*

Department of Civil and Environmental Engineering, Temple University, Philadelphia, PA 19122, phone (215)204-4807, email: hjzhang@temple.edu

## Background & Objectives

A common function group in organic contaminants is nitrogen-oxygen bond (R<sub>1</sub>R<sub>2</sub>N-OR<sub>3</sub>), and examples include aromatic *N*-oxides, oximes, isoxazoles and hydroxylamines. Specifically, aromatic *N*-oxides are widely used as veterinary antibacterial agents and growth promoters, and have been considered as potential carcinogens.<sup>1</sup> Oximes, heavily used as pesticides in agriculture, are highly toxic to mammals.<sup>2</sup> Isoxazolyl is commonly found in bacteriostatic agents, which can lead to contamination of soils and waters while released.<sup>3</sup> Various studies have reported that reductive transformation can be one of the dominant transformation pathways for N-O containing compounds (NOCs) in reducing sediments and aquifers. However, there is a lack of mechanistic understanding of the reductive behaviors of NOCs. To this end, a systematic study was carried out to investigate reduction of a number of different NOCs; the overall goal is to develop predictive models that are necessary to evaluate the fate and risks of structurally-related environmental contaminants.

Aqueous Fe<sup>II</sup> has been observed to quickly reduce a number of organic contaminants.<sup>4</sup> Meanwhile, Fe<sup>II</sup>-organic ligand complexes are reported to be much more reactive due to their fast redox reactivity.<sup>5</sup> Therefore, dissolved Fe<sup>II</sup> and Fe<sup>II</sup>-tiron complex will both likely contribute to the reductive transformation of NOCs.

In this project, the reduction kinetics and mechanisms of carbadox (CDX), sulfamethoxazole (SMX) and several model NOCs in the presence of dissolved Fe<sup>II</sup> and Fe<sup>II</sup>-tiron complex were examined. The major degradation processes were found to be the cleavage of the nitrogen-oxygen bond. Computational calculations were performed to understand the rate-limiting steps for each type of reduction, as well as the sequence of electron transfer and protonation. Based on the observed kinetics, reduction products and calculated reaction net energies, the reduction mechanisms of various NOCs by aqueous Fe<sup>II</sup> or Fe<sup>II</sup>-tiron complex were proposed.

## Materials & Methods

### (a) Kinetic Experiments

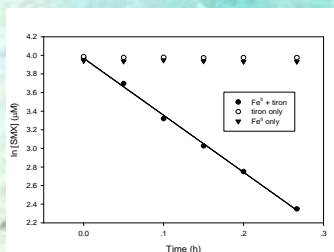
- All solutions were prepared inside an oxygen-free glovebox (95% N<sub>2</sub>, 5% H<sub>2</sub>, Pd catalyst).
- Decreases in the concentrations of NOCs were monitored by HPLC.
- Reaction products were analyzed by HPLC/QToF-MS.

### (b) Computational Calculation

- Performed by the Gaussian 09 software package.
- Structural optimizations were carried out by the density functional (B3LYP) theory.
- The 6-31++G(d) + LANL2DZ mixed basis set was used for NOCs complexed with Fe<sup>II</sup>, and the 6-31++G(d) basis set was used for all the other calculations.

## Results & Discussion

### A. Reduction kinetics of SMX by Fe<sup>II</sup>-tiron complex



Reaction conditions: 50 μM SMX, 0.5 mM Fe<sup>II</sup>, 10 mM tiron, pH 7.50, I = 0.2M.

## Results & Discussion (Continued)

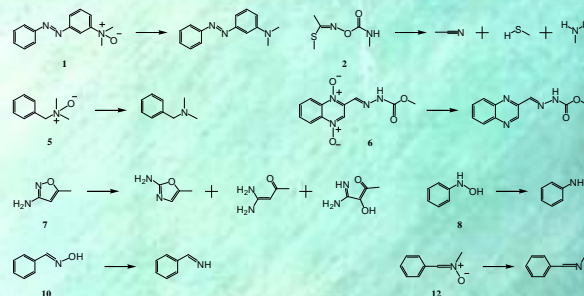
### B. Structures, physical-chemical properties, and *k*<sub>obs</sub> of the selected NOCs

#	Structure	<i>k</i> <sub>obs</sub> (h <sup>-1</sup> )	BDE (eV)	EA (eV)	N-O bond length (Å)	
					neutral	anion
1		4.134 <sup>a</sup>	5.206	3.201	1.380	1.384
2		0.013 <sup>a</sup>	3.518	4.232	1.420	-
3		0.0046 <sup>a</sup>	3.440	2.562	1.410	1.491
4		0.00084 <sup>a</sup>	3.564	2.818	1.427	1.411
5		0.0002 <sup>a</sup> 67.91 <sup>b</sup>	5.258	1.963	1.380	1.430
6		11.50 <sup>a</sup>	N1-O: 5.570 N4-O: 5.537	3.352	N1-O: 1.294 N4-O: 1.295	N3-O: 1.328 N4-O: 1.327
7		130.77 <sup>d</sup>	9.422	0.804	1.429	1.487
8		53.84 <sup>d</sup>	3.674	0.774	1.411	1.421
9		1.43 <sup>d</sup>	11.391	2.669	1.407	1.397
10		0.002 <sup>d</sup>	4.741	2.001	1.406	1.463
11		0.001 <sup>d</sup>	5.747	1.891	1.311	1.360
12		0.00007 <sup>d</sup>	5.821	2.194	1.300	1.349
13		no reaction <sup>d</sup>	3.143	0.703	1.433	1.441

Reaction conditions: a: 0.5 mM Fe<sup>II</sup>, no tiron, 25 μM NOC, 25 mM buffer, pH 5.50, I = 0.1 M.<sup>3,6</sup> b - d: 0.5 mM Fe<sup>II</sup>, 10 mM tiron, 50 μM NOC, 50 mM buffer, I = 0.2 M (pH = 5.00 for b, pH = 6.00 for c, pH = 7.00 for d).

- The order of the observed reaction rate constants is: phenyl *N*-oxide >> aliphatic oxime > aliphatic *N*-oxide >> aromatic *N*-oxide with side chain >> isoxazole >> phenyl hydroxylamine > aromatic oxime > aromatic *N*-oxide without side chain > alkenyl *N*-oxide.

### C. Product analysis of NOCs

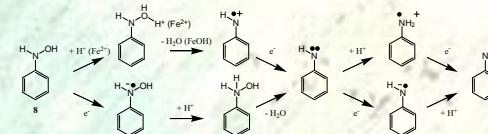


- The products of *N*-oxides and oximes<sup>7</sup> are formed by dissociation of N-O bonds.
- The degradation of isoxazole involves the rearrange of the aromatic ring and the dissociation of N-O bond<sup>8</sup>.

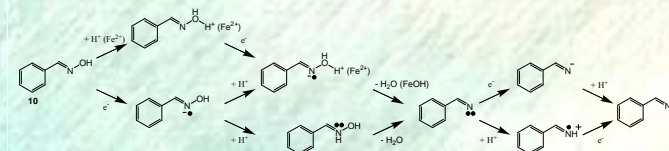
## Results & Discussion (Continued)

### D. Proposed mechanisms based on product analysis & computational calculation

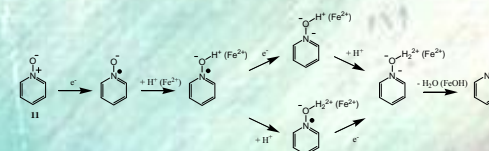
#### a. Proposed mechanism for reduction of 8 by Fe<sup>II</sup>-tiron:



#### b. Proposed mechanism for reduction of 10 by Fe<sup>II</sup>-tiron:



#### c. Proposed mechanism for reduction of 11 by Fe<sup>II</sup>-tiron:



## Conclusions

- The products of *N*-oxides and oximes are their respective deoxygenated analogs, while reduction of isoxazole involves rearrangement of the aromatic ring and cleavage of the N-O bond.
- The electron withdrawing substituents of the NOCs can highly facilitate the N-O bond breaking.
- Complexation of the NOCs by soluble Fe<sup>II</sup> can yield higher reactivity than protonation of the NOCs.
- The sequence of electron transfer and protonation/complexation is different among various NOCs.
- The EA can provide a good quality correlation with log *k* if the first electron transfer is the rate-limiting step for certain NOCs. Meanwhile, linear correlation between BDE and log *k* will be observed if the N-O bond cleavage is rate-limiting. Protonation can also be the rate-limiting step for some categories of NOCs.

## References

- (1) Albini, A.; Pietra, S. *Heterocyclic N-oxides*; CRC Press: Boston, 1991.
- (2) Hassell, K. A. *Macmillan Press: Basingstoke, U.K.*, 1991.
- (3) Kenneke, J. F.; Weber, E. J. *Environ. Sci. Technol.* **2003**, 37, 713.
- (4) Strathmann, T. J.; Stone, A. T. *Environ. Sci. Technol.* **2001**, 35, 2461.
- (5) Bussan, A. L.; Strathmann, T. J. *Environ. Sci. Technol.* **2007**, 41, 6740.
- (6) Strathmann, T. J.; Stone, A. T. *Environ. Sci. Technol.* **2002**, 36, 5172.
- (7) Strathmann, T. J.; Stone, A. T. *Environ. Sci. Technol.* **2001**, 35, 2461.
- (8) Mohatt, J. L.; Strathmann, T. J. *Environ. Sci. Technol.* **2011**, 45, 4793.

## Acknowledgements

- The authors are thankful to Drs. Michael L. Klein and Hao Dong at the Temple University for computational calculation.