# Green Chemistry and Life Cycle Thinking

Terry Collins

EPA Pollution Prevention through Nanotechnology Conference

*Arlington, VA, September 26, 2007*

# Greening Oxidation Chemistry

Replace chlorine technologies with alternatives based on Nature's oxidants oxygen or hydrogen peroxide

Develop oxidation catalysts for oxygen or hydrogen peroxide comprised of the common elements of biochemistry—C, H, O, N, Fe

# Designing Solutions for Catalyst Degradations for 20+ years

**1.** Design ligand system thought to be suitable and make metal complex

**2.** Oxidize complex until ligand decays

**3.** Characterize degradation products and identify weak site

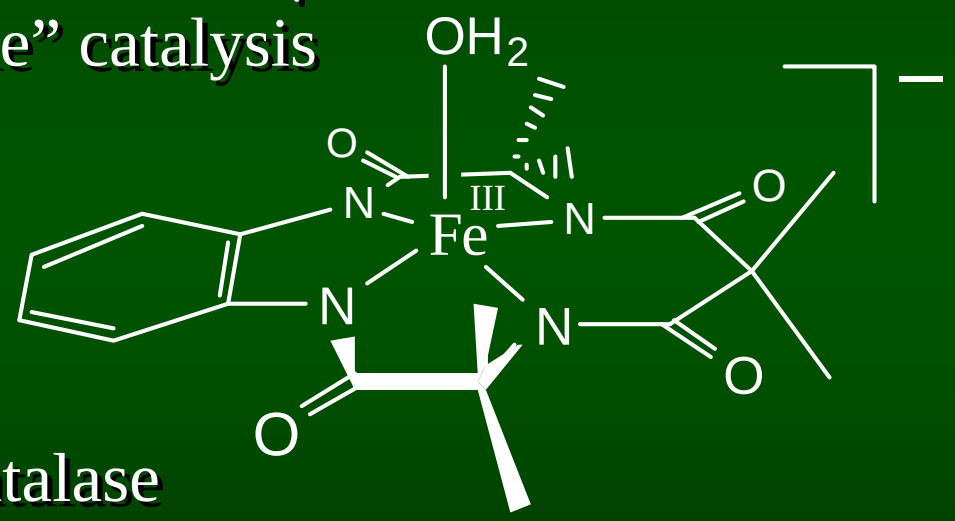
**4.** Modify weak site to be more robust


Designing Ligands for Oxidizing Complexes, T. J. Collins *Accounts Chem. Res.*, **1994**, *27*, 279-285.

TAML® Oxidant Activators: A New Approach to the Activation of $H_2O_2$ for Environmentally Significant Problems, T. J. Collins *Accounts Chem. Res.*, **2002**, *35*, 782-790.

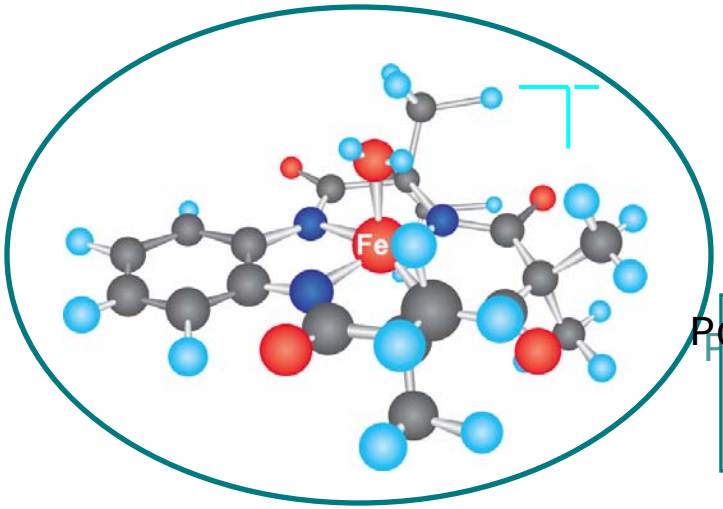
# TAML® Catalyst Features

- biochemically common elements — prototype v. low toxicity
- effective at 0.1 to 4 ppm = nM to low μM
- beginning of "dial-a-lifetime" catalysis
- economical to synthesize
- water-soluble
- usable from pH 1 to 14.5
- efficient users of peroxide
  —fast peroxidase/slow catalase
- >100 patents
- two licenses in place; >100 kg produced
- >100 companies have CDA with Carnegie Mellon University
- GreenOx Catalysts, Inc. — next step: multi-ton production



## Extensive Scientific Characterization of TAML® Activators and Their Chemistry

TAML activators solve a 6-decade standing chemistry problem. They work as well as nature's major oxidizing enzymes. Overall, we understand very well how they work.




**Water Cleaning**
chlorinated pollutants, EDCs, phenols, BPA, …

**Textiles**
dye bleaching, effluent decolorization

**Biological Warfare**
Rapid destruction of anthrax-like spores

**Possible Site Cleaning**
all the problem compounds of the TNT explosives

**Pesticides Decon**
major class (thiophosphates) rapidly/completely destroyed

**Pulp and Paper**
pulp bleaching, effluent smell, organochlorine and color removal

**Military Chemical**
rapid destruction of toxic residuals & CWAs

**Laundry**
dye transfer inhibition, stain removal

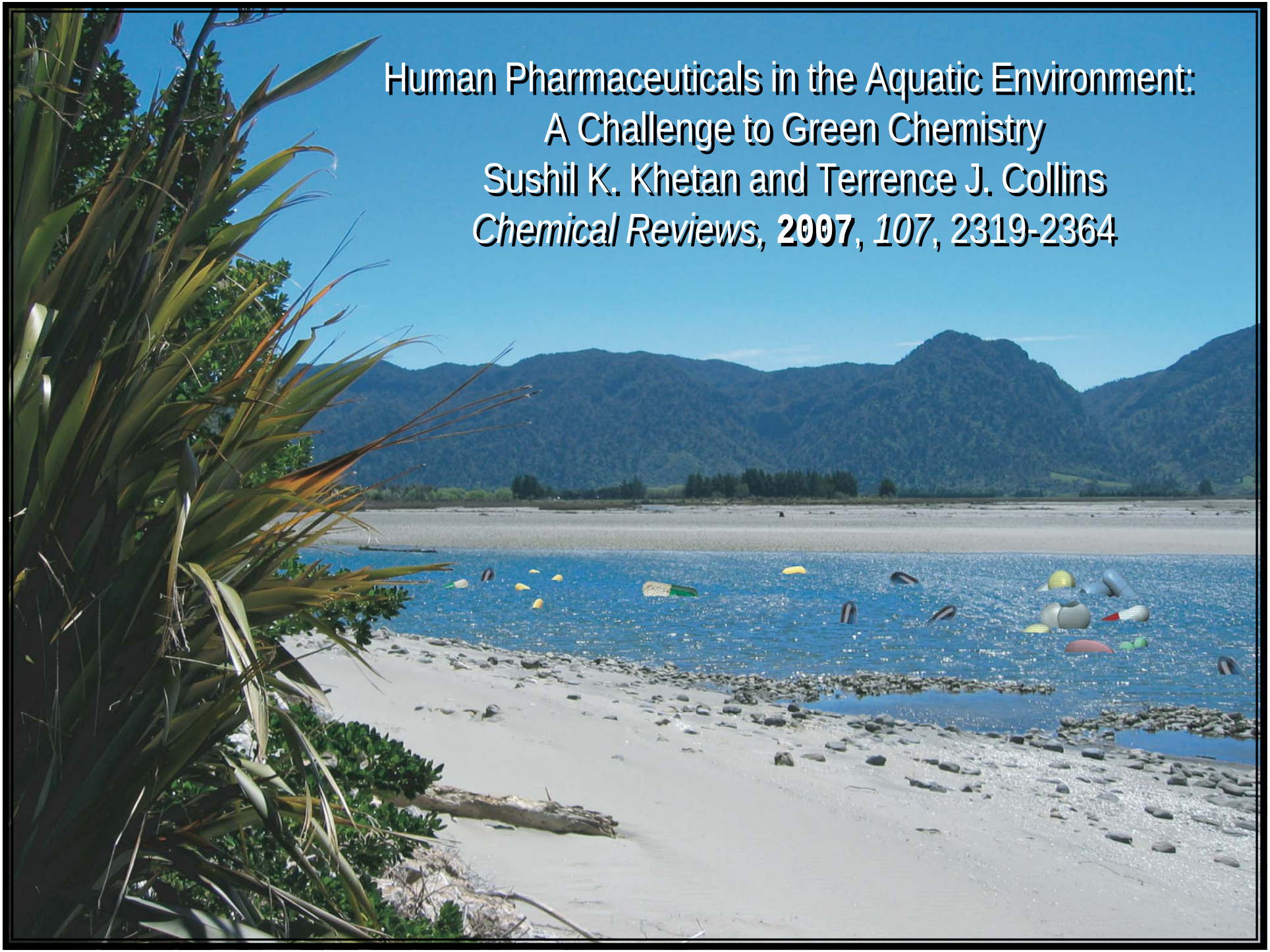
**Pharmaceuticals Decon**
trace pharmaceuticals removed from water

**Agricultural**
removal of estrogens from water, renewable feedstocks

**Drinking Water Disinfection**
safer drinking water free of chlorinated disinfection byproducts

**Others**
metal refining, carpet recycling, hospital disinfection

**Petroleum Refining**
removal of sulfur from diesel & gasoline



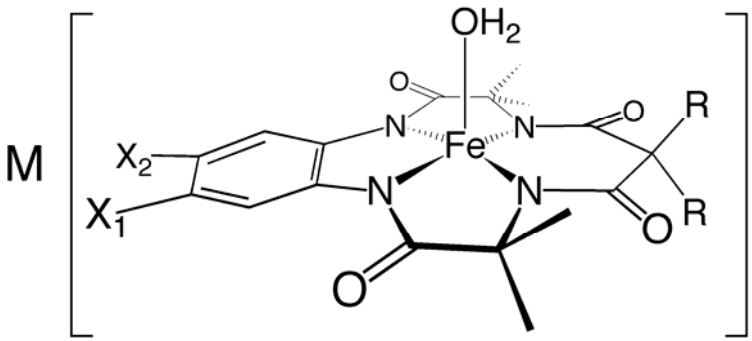
# Human Pharmaceuticals in the Aquatic Environment: A Challenge to Green Chemistry

Sushil K. Khetan and Terrence J. Collins

*Chemical Reviews*, **2007**, *107*, 2319-2364

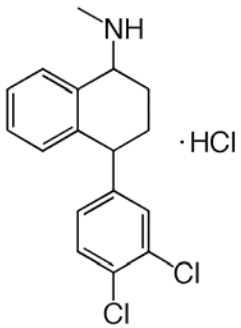
# Fe-TAML/$H_2O_2$ Readily Decomposes APIs

Yan Xiang Delia Popescu Melanie Vrabel Peter Madsen, Jr Evan Beach

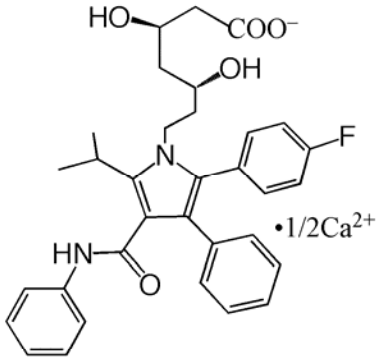



Fe-B*: $X_1 = X_2 = H$, $R = CH_3$

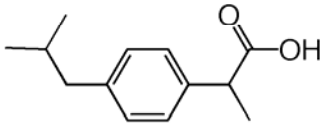
Fe-DCBF$_2$: $X_1 = X_2 = Cl$, $R = F$



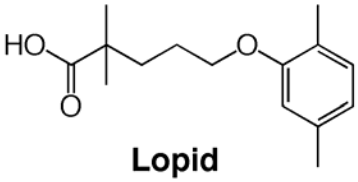

**Zoloft**



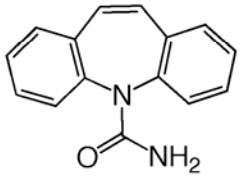

**Lipitor**



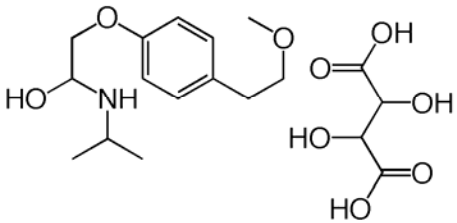

**Ibuprofen**



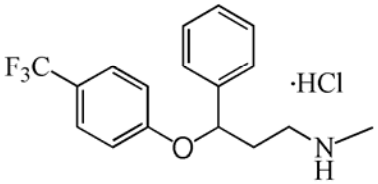

**Lopid**



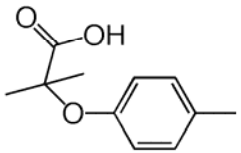

**Carbamazepine**




**Lopressor**

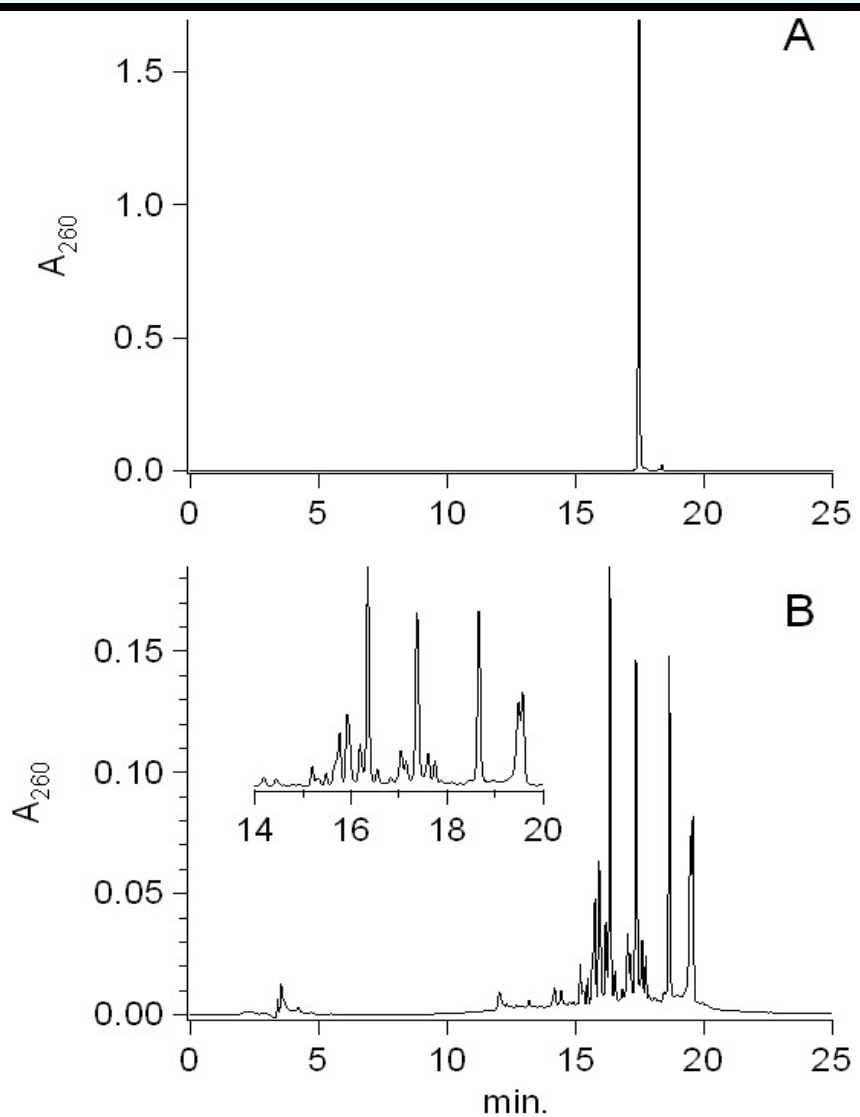



**Prozac**




**Clofibric Acid**

Atorvastatin-calcium shows 100% degradation in 2 min. At least 40 products are observed by HPLC (>20 characterized). Similar degradation results were shown at low ppm concentrations at longer reaction times.




## *Reaction Conditions:*

- [Atorvastatin] = 10 μM
- [Fe-TAML] = 100 nM *(using very aggressive Fe-TAML—works more slowly with prototype)*
- [$H_2O_2$] = 1.6 mM *(ca. 1.5 mineralization requirement)*
- 0.01 M carbonate buffer
- 25°C

## *Research Methods*

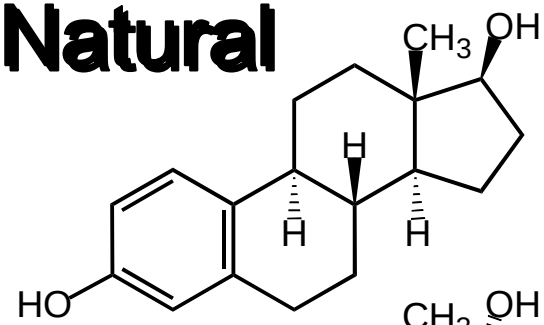
HPLC-ESI-MS-MS , UV-Vis, HPLC, $^{19}$F- $^{1}$H- $^{13}$C-NMR, IC

# Degradation of Natural & Anthropogenic Estrogens

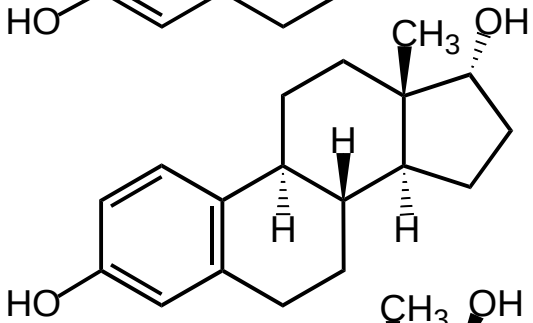
Nancy Shappell Delia Popescu Peter Madsen, Jr. Melanie Vrabel

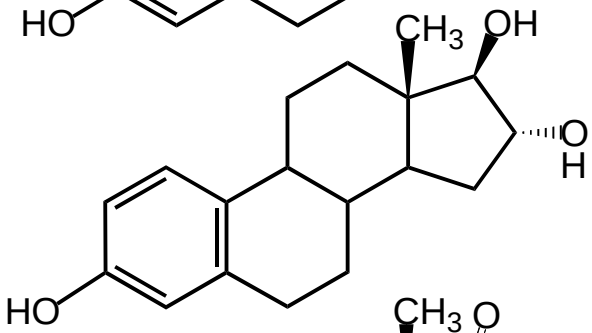
# Estrogenic Substrates and Testosterone

## Natural

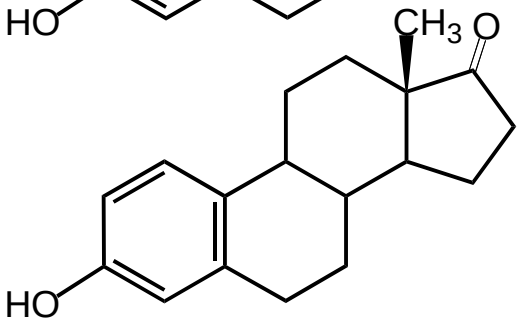



**Estradiol (E2)**
17-β mw 272
Most Potent 1X
17-α 0.1X

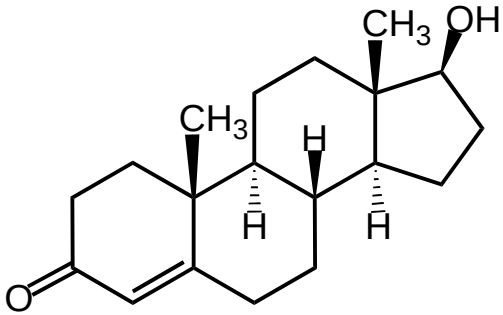



**Estriol (E3)**
mw 288
0.1X

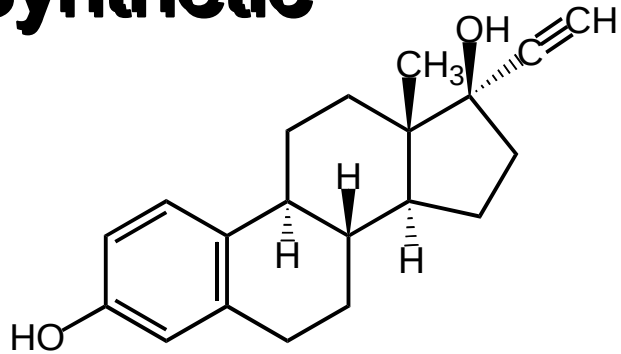



**Estrone (E1)**
mw 270
0.01X




**Testosterone**

## Synthetic

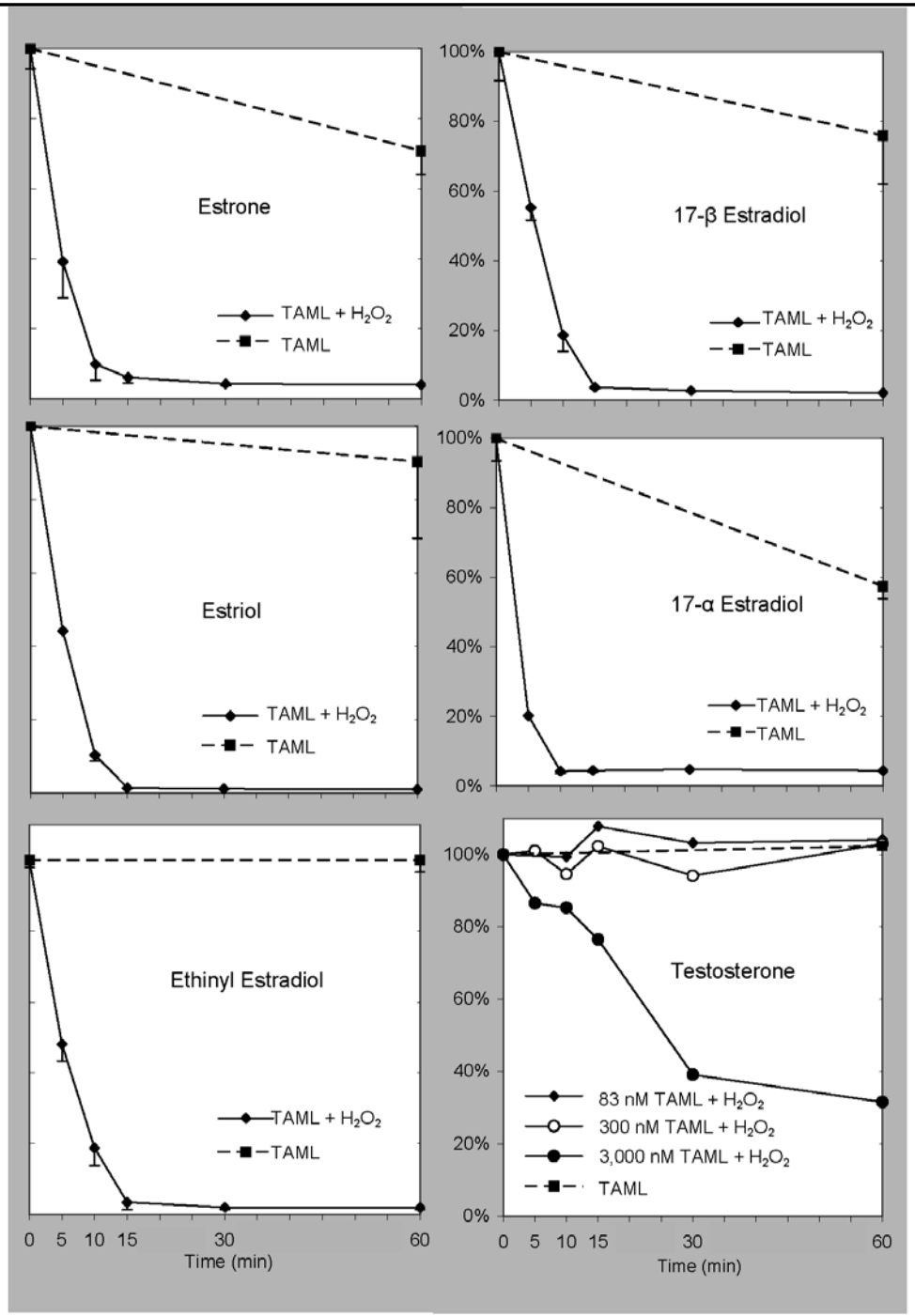



**Ethinyl Estradiol (EE2)**
mw 296 ca. 1X

# Degradation of steroids by Fe-B*/$H_2O_2$ (LCMS/MS)

- Steroid = 80 μM
- FeB* = 83 nM
- $H_2O_2$ = 4 mM
- pH = 8
- Catalase termination

**In a preliminary experiment, incubations with a municipal wastewater sample (obtained prior to chlorination) resulted in >99% removal of estradiol (ELISA).**

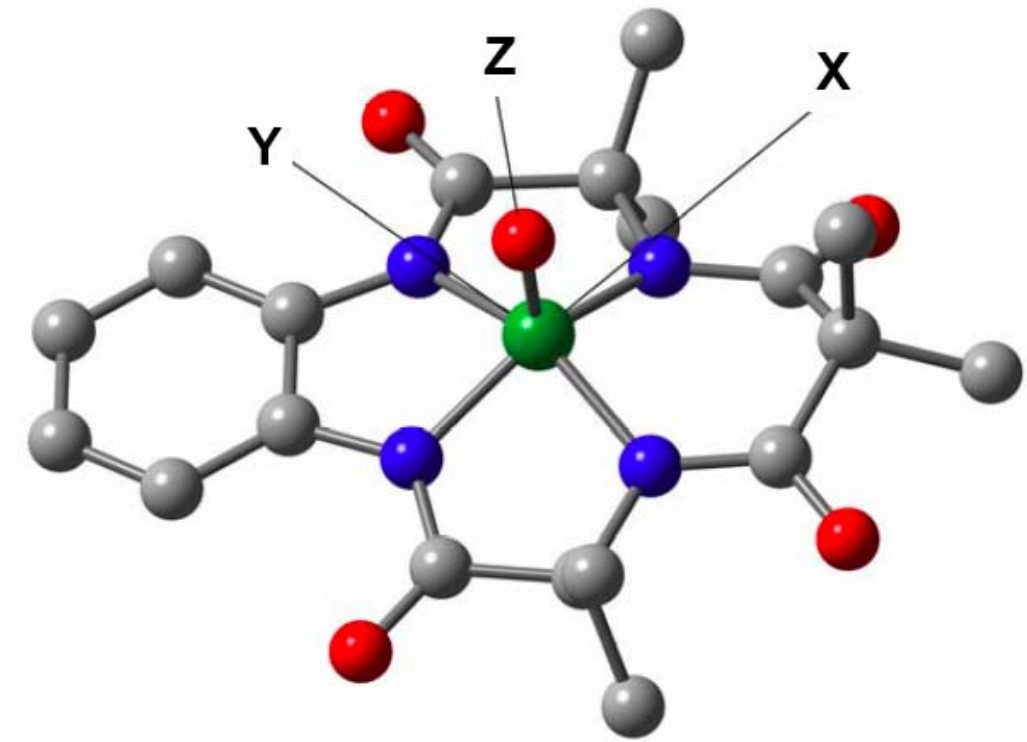


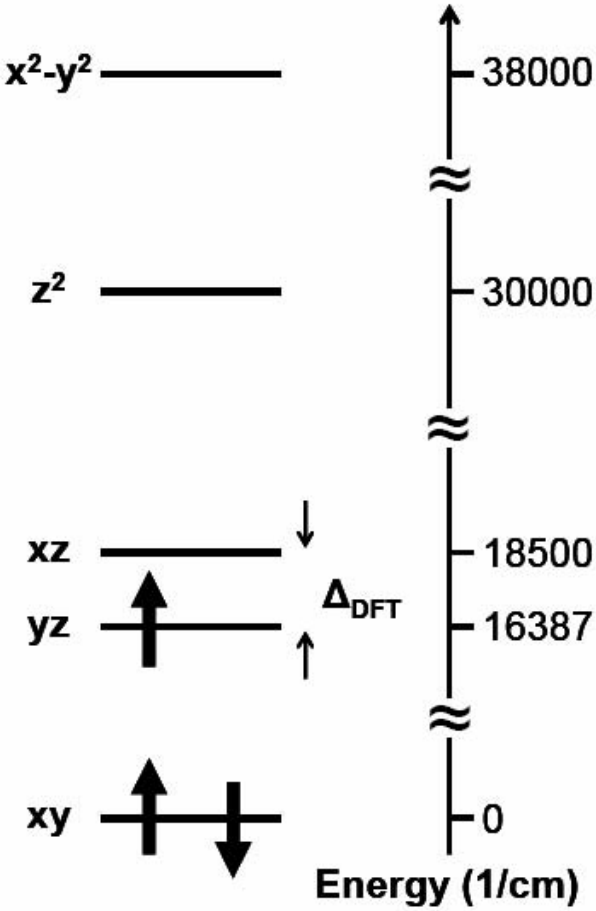

Nancy Shappell et al. USDA

# DFT Calculations to Model EPR and Mössbauer Properties of Final Product

Emile Bominaar Eckard Münck Filipe Tiago de Oliveria Arani Chanda

Chemical and Spectroscopic Evidence for an FeV-Oxo Complex, F. Tiago de Oliveira, A. Chanda, D. Banerjee, X. Shan, S. Mondal, L. Que Jr., E. L. Bominaar, E. Münck, T. J. Collins, *Science*, **2007**, *315*, 835-838.



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