

***OXIDATION IN CATALYSIS  
AND GREEN CHEMISTRY***

**Andreja Bakac**

**Ames Laboratory, Iowa State University**

# OXIDATION

## Importance:

- *Industry*
- *Environment*
- *Biology*

## Options

- *Strong oxidants (corrosive, unsafe, difficult to handle, large disposal cost)*
- *Forcing conditions (high temperature, concentrations, pressure)*
- *Use (develop) catalysts*

## **IDEAL OXIDANT: AIR OR O<sub>2</sub>**

- **ABUNDANT**  
*Practically no cost*
- **NON-TOXIC**  
*Easily handled*
- **FINAL PRODUCT IS WATER**  
*Safe for environment*  
*No disposal cost*
- **HAS POTENTIAL TO OXIDIZE MANY SUBSTRATES**  
*Useful for many applications*

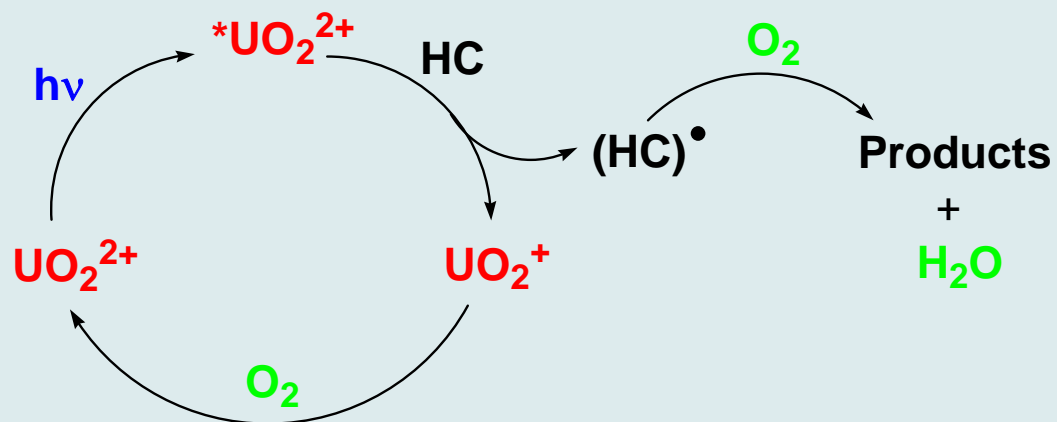
***But:***

- ***Does not react readily (good for life on earth)***
- ***Needs to be activated***

# I. URANYL-BASED PHOTOCATALYTIC OXIDATIONS

Uses  $O_2$  as oxidant

Light: visible and near-UV



**Excited state:**

- Long lived
- Extremely oxidizing

## ***POTENTIAL FOR USE IN WASTE TREATMENT***

### **Substrates that can be oxidized with O<sub>2</sub>**

- Alcohols
- Aldehydes
- Ethers
- Alkanes (except methane !)
- Many others

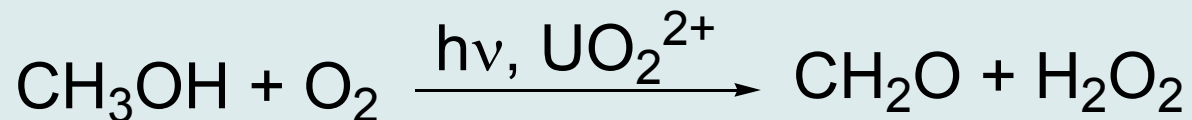
### **Replace O<sub>2</sub> by H<sub>2</sub>O<sub>2</sub>**

Oxidize benzene to phenol with high quantum yield

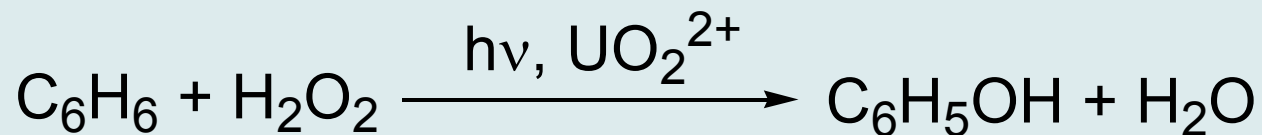
- *Depleted uranium abundant at DOE sites*
- *Method works at ambient temperatures and pressures*
- *Minimize escape of volatile contaminants to environment*

## COOPERATIVITY IN MULTICOMPONENT SYSTEMS

*Some substrates can be oxidized with O<sub>2</sub>:*



*Others (benzene) require H<sub>2</sub>O<sub>2</sub>*



*Mixture: generates its own H<sub>2</sub>O<sub>2</sub>*

*reduces requirement for externally added oxidant*

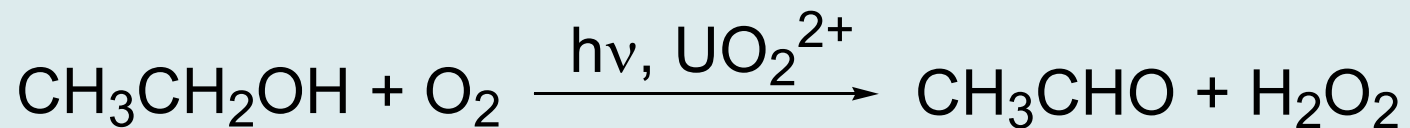
## **MIXED WASTES**

***Radioactive (uranyl) + nonradioactive wastes:  
Have all components for photooxidation***

***Develop method / conditions to utilize  $\text{UO}_2^{2+}$   
Oxidize organics***

***Now have low level radioactive waste***

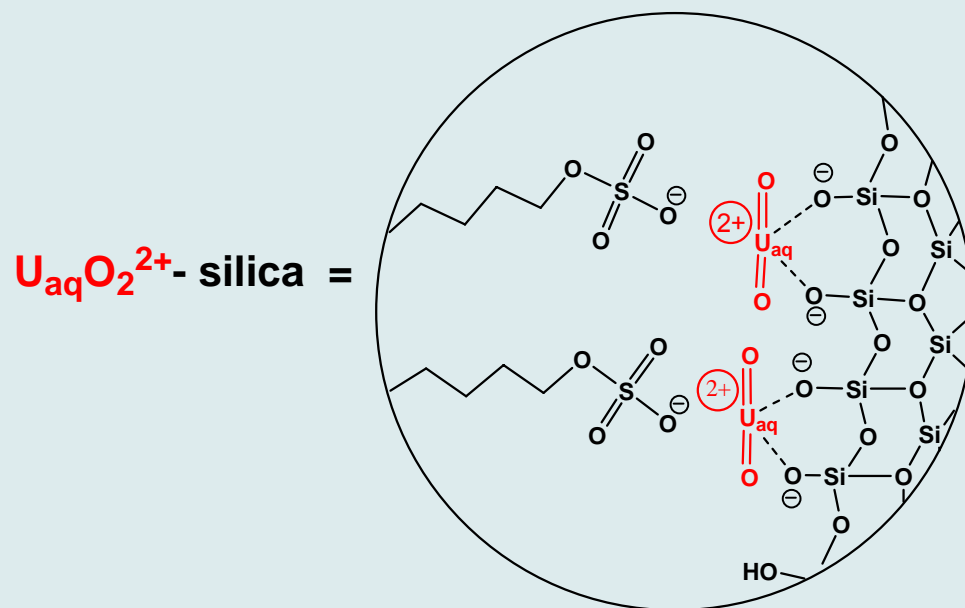
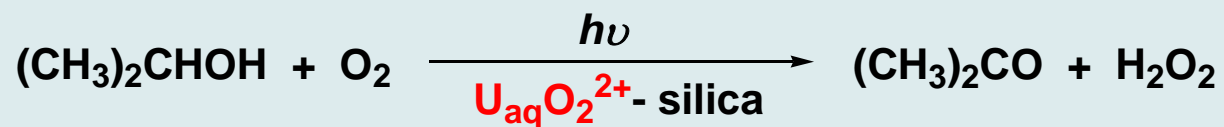
## ***THE OTHER PRODUCT- H<sub>2</sub>O<sub>2</sub>***



### ***MECHANISTIC STUDIES:***

- Even as H<sub>2</sub>O<sub>2</sub> accumulates, reaction still uses O<sub>2</sub> (NOT H<sub>2</sub>O<sub>2</sub>)
- As long as [C<sub>2</sub>H<sub>5</sub>OH] > [H<sub>2</sub>O<sub>2</sub>], H<sub>2</sub>O<sub>2</sub> will keep accumulating

# URANYL SUPPORTED ON MESOPOROUS SILICA



Active in oxidation of alcohols with  $\text{O}_2$

## Kinetics ( $k/M^{-1} s^{-1}$ ) of Quenching of Excited Uranyl Ions with Alcohols

Substrate	$U_{aq}O_2^{2+}/H_3PO_4^a$	$U_{aq}O_2^{2+}/H_2O^b$	$U_{aq}O_2^{2+}{}^c$	$U_{aq}O_2^{2+}/\text{silica}^{d, e, f}$	$U_{aq}O_2^{2+} + SiO_2^{c, g}$
MeOH	$1.5 \times 10^6$ <sup>h</sup>	$6.4 \times 10^6$		$7.3 \times 10^5$	
2-PrOH	$1.4 \times 10^7$ <sup>h</sup>	$8.5 \times 10^7$	$3.1 \times 10^5$	$1.3 \times 10^7$	$1.7 \times 10^5$
2-BuOH	$1.7 \times 10^7$			$1.7 \times 10^7$	
2-Pentanol	$1.8 \times 10^7$			$1.5 \times 10^7$	
tert-BuOH	$1.4 \times 10^5$			$1.2 \times 10^5$	
none <sup>i</sup>	$1.0 \times 10^4$	$8.3 \times 10^5$	$4.0 \times 10^4$	$1.5 \times 10^4$	$3.7 \times 10^4$

<sup>a</sup> 0.6 M aqueous  $H_3PO_4$ . <sup>b</sup> In water at natural pH (~7).

<sup>c</sup> In water + 1.0 mM NaOH added. U-content: 0.6 mM. Measured pH = 5.

<sup>d</sup> 1 mM NaOH added. Measured pH ~ 5, see text.

<sup>e</sup>  $U_{aq}O_2^{2+}$  on mesoporous silica. <sup>f</sup> At [alcohol]  $\leq$  15 mM, see text.

<sup>g</sup> Aqueous  $U_{aq}O_2^{2+} +$  silica gel. <sup>i</sup> Self decay rate constants in units of  $s^{-1}$ .

**Reactivity comparable to solution species**

## II. IRON(II)-CATALYZED OXIDATIONS BY OZONE



### Oxidation of organic matter:

- *Biological and catalytic oxidations require catalysts*

*Often iron-based*

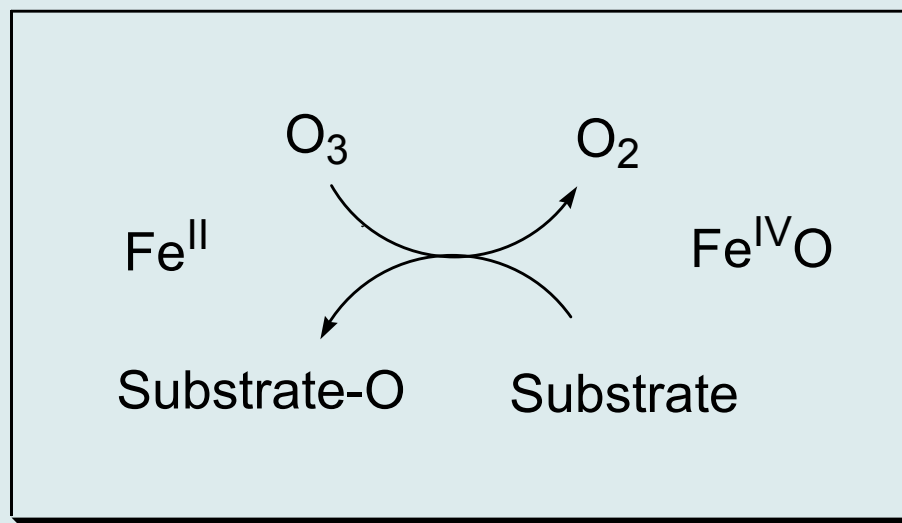
*Often complex (enzymes) and fragile*

### Ozone:

- *Potent oxidant*
- *Reacts readily with organic matter*
- *Used for water purification and food treatment*
- *Not always fast*
- *No catalysts are used (would not survive?)*
- *Catalysts would be advantageous*

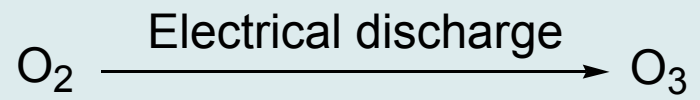
## **$Fe^{IV}/Fe^{II}$ COUPLE PREFERRED FOR OXIDATION OF ORGANIC SUBSTRATES**

**Ideally:**

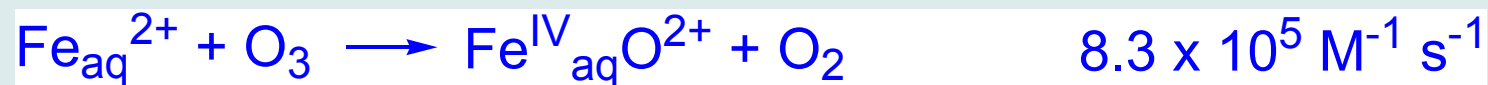


***Avoid 1-electron processes  
(e. g. Fenton chemistry with  $H_2O_2$ )***

# OZONE GENERATOR

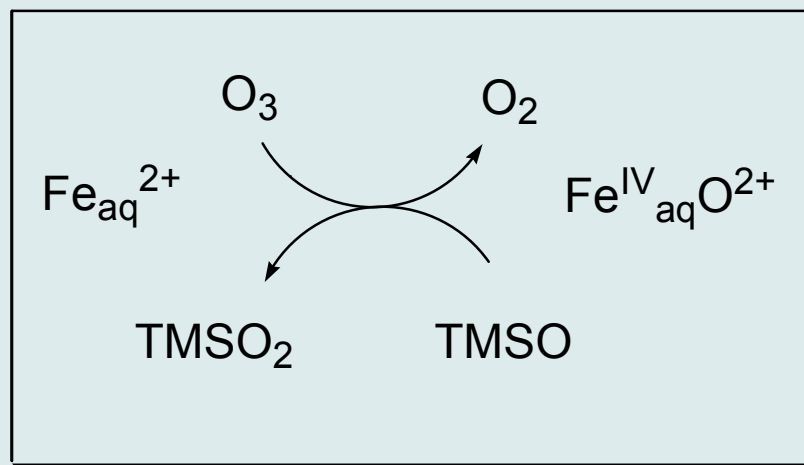


## AQUEOUS $\text{Fe}_{\text{aq}}^{2+}$ -OZONE REACTION

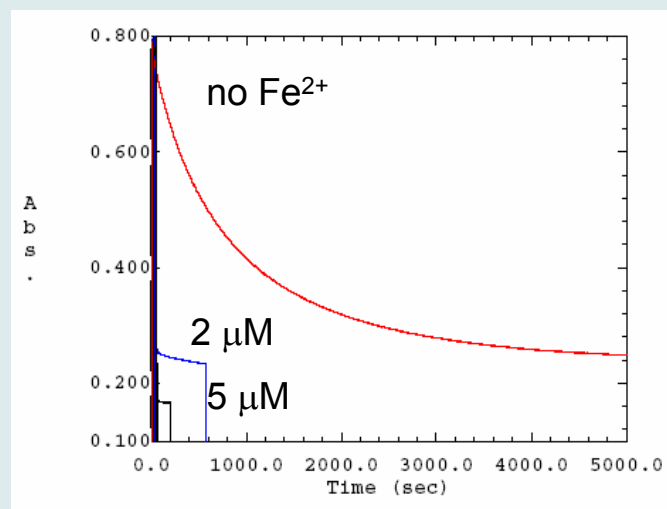


- *At equimolar  $\text{Fe}_{\text{aq}}^{2+}$  and  $\text{O}_3$ , yields of  $\text{Fe}_{\text{aq}}\text{O}^{2+}$  are ~quantitative*
- *$\text{Fe}_{\text{aq}}\text{O}^{2+}$  reacts rapidly with organic substrates:*
  - *Alcohols*
  - *Ethers*
  - *Aldehydes*
  - *Nitriles*
  - *Sulfides*
  - *Sulfoxides*

# $Fe^{2+}$ -CATALYZED OXIDATION OF TMSO WITH $O_3$



$[Fe_{aq}^{2+}] = 0 - 5 \mu M$   
 $[TMSO] = 100 \mu M$   
 $[O_3] = 100 \mu M$   
 $[HClO_4] = 0.10 M$   
 $25^\circ C, \lambda = 240 nm$



## SUMMARY

Uranyl is a good catalyst for oxidations with air and light

- *Oxidizes variety of substrates*
- *Generates hydrogen peroxide for other uses*
- *Supported catalyst is as effective as solution species*

Oxidations with ozone

- *Produced easily and cleanly (requires electricity)*
- *Clean (oxygen is product)*
- *$\text{Fe}_{\text{aq}}^{2+}$  is good catalyst*

## **COLLABORATORS**

*Dr. Yun Mao*

*Dr. Wei Dong Wang*

*Dr. Oleg Pestovsky*

*Dr. Victor Lin*

*Dr. Kelemu Lemma*

*Ms. Jennifer Nieweg*

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