Advanced Oxidation Processes

(AOP)

For Water and Wastewater Treatment

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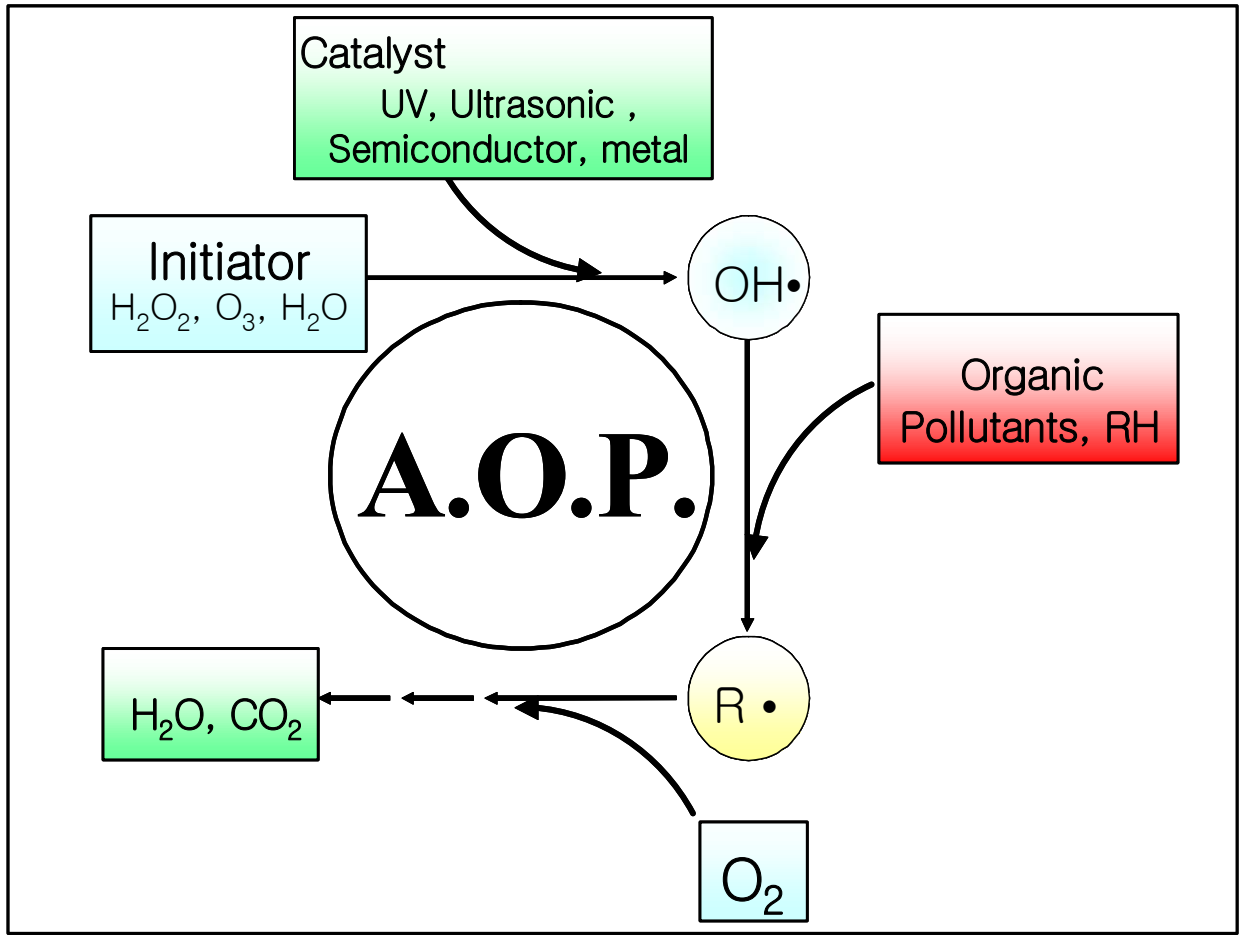
Advanced Oxidation Processes (AOPs)

AOPs: involves the *in-situ* generation of highly potent chemical oxidants such as the hydroxyl radical (•OH) for accelerating the oxidation and hence destruction of a wide range of organic contaminants in polluted water and air



Reactivity of hydroxyl radical (•OH)

- High redox potential (2.80 V)
- nonslectively very reactive, and rapid reaction with various organic substrates (diffusion controlled rate)
- eletrophilic

Redox Potentials of selected oxidants (V vs NHE)

•OH	**2.80**
O_3	**2.07**
H_2O_2	**1.78**
HO_2 ·	**1.70**
ClO_2	**1.57**
HOCl	**1.49**
Cl_2	**1.36**

Rate constants for selected reactions of •OH in aqueous solution (M^{-1} s^{-1})

•OH + MeOH →	1×10^9
•OH + EtOH →	2×10^9
•OH + Phenol →	6.6×10^9
•OH + 2,4-D →	3×10^9
•OH + Prolline →	3.1×10^8
…	

Reactivity of hydroxyl radical (•OH)

~ at high pH (>12, pKa ($^{\bullet}$OH = 11.8), it deprotonates.

~ an important difference between OH radical and $O^{\bullet -}$ is their reactivity toward to O_2

Three types of reactions

(1) Addition to C-C and C-N doubles bonds

~ not with C-O double bonds (which is electron deficient carbon)

~ regioselective largely due to its electrophilic nature

(2) H-abstraction

~ a considerable driving force for H-abstraction reactions by $^{\bullet}$OH

~ primary hydrogens ($-CH_3$) are less likely abstracted than secondary (-CH2-) and tertiary(-CH-) ones

~ neighboring substituents stabilizing the resulting radical

(3) Electron transfer

~ direct ET is rarely observed in $^{\bullet}$OH-reactions

Mineralization of organic pollutant in AOP

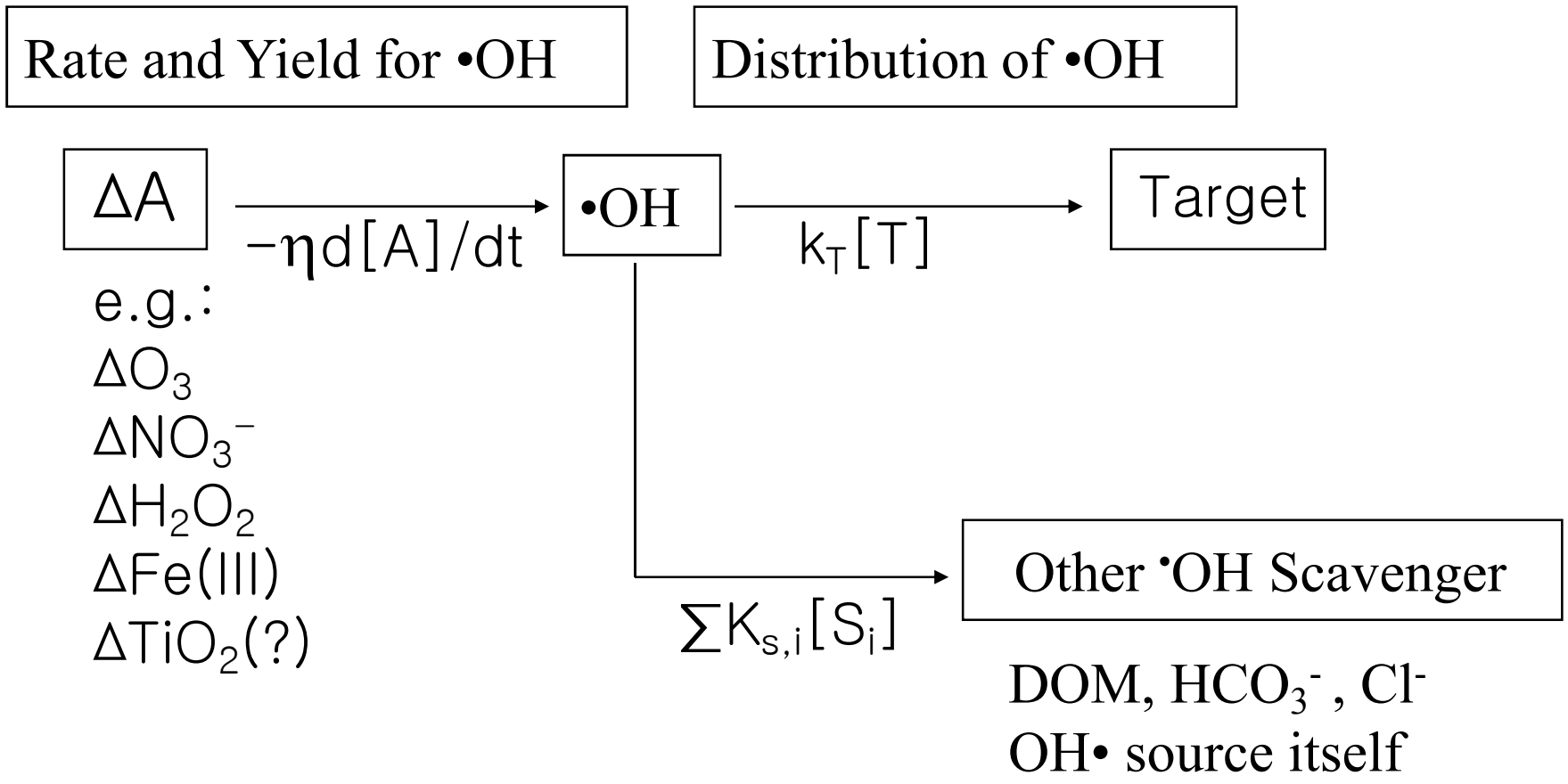
$$RH + {}^{\bullet}OH \rightarrow R^{\bullet} + H_2O$$ **Hydrogen atom abstraction**

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}$$

$$RO_2^{\bullet} + RO_2^{\bullet} \rightarrow [RO_4R] \rightarrow\rightarrow ROH + R`COR` + R`COH$$

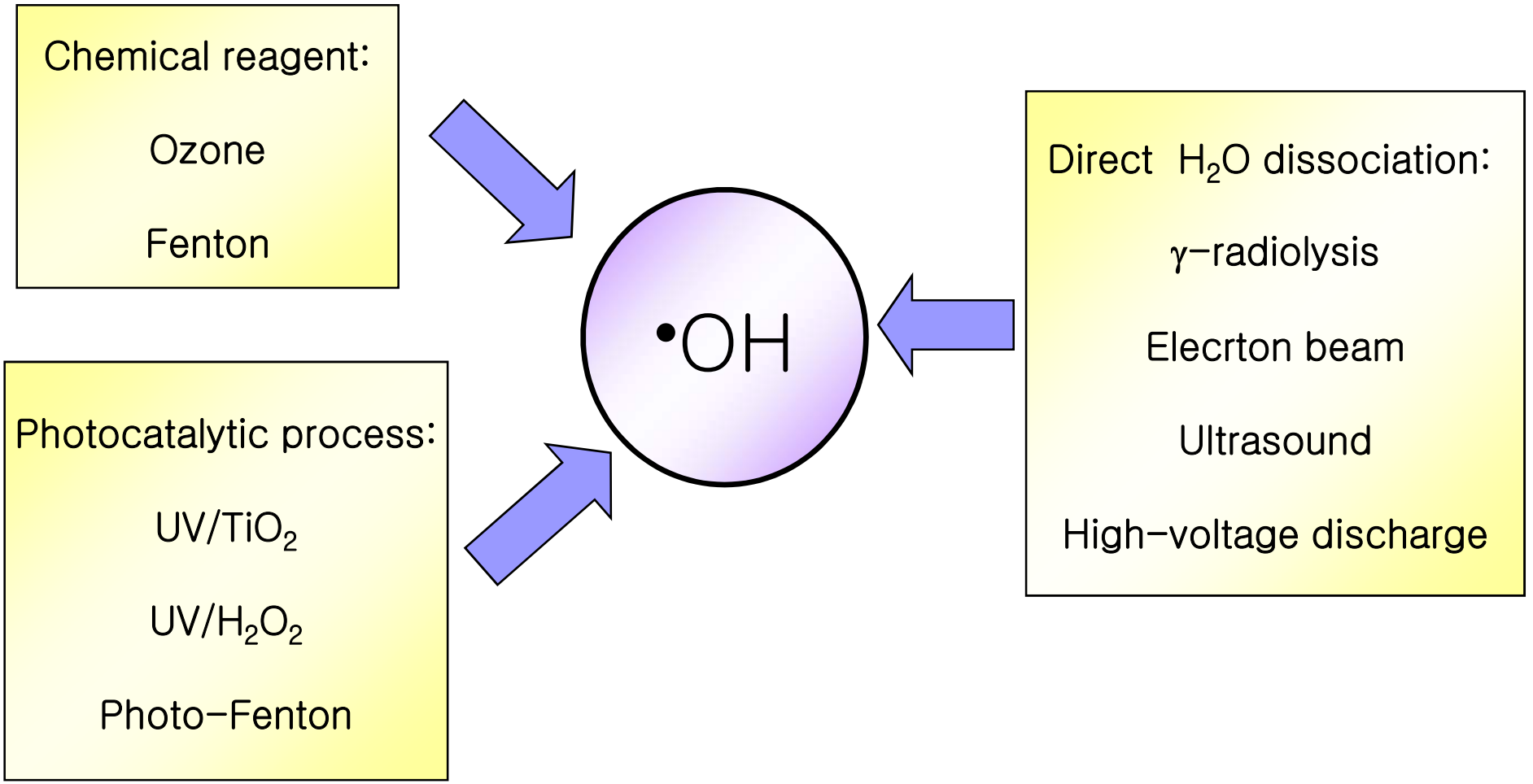
$$\begin{array}{l} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad + {}^{\bullet}OH \downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad O_2 \downarrow \\ \qquad\qquad\qquad\qquad\qquad + {}^{\bullet}OH / O_2 \\ CO_2 + H_2O \quad \leftarrow\leftarrow \quad R``COOH \end{array}$$

Key parameters in AOP



Classification of AOP

- **Depending upon the way of generating hydroxyl radical: •OH**



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