ART Advanced Redox Technology (ART) Lab
고도산화환원 환경공학 연구실

http://artlab.re.kr

Advanced Oxidation Process

(Properties and Analysis of OH Radical)

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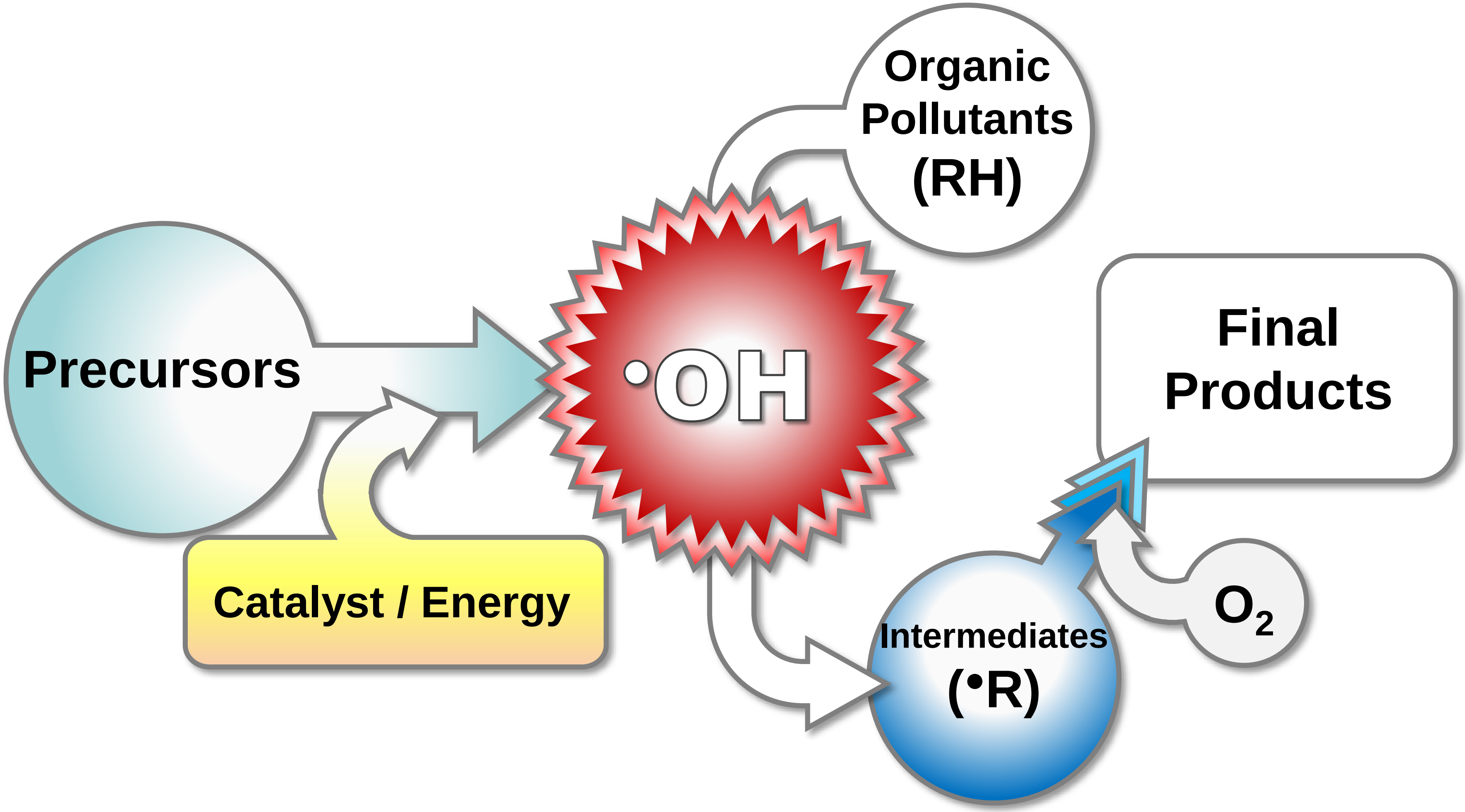
What is "Advanced Oxidation Process" ?

AOP (or AOT): Water treatment process (or technology) utilizing hydroxyl radical (•OH), a nonselective oxidizing radical species



Oxidants for Water Treatment

Standard Redox Potential (V_{NHE})

$^{\bullet}OH$ ($E^0(^{\bullet}OH/OH^-)$ = +2.8 V_{NHE}; 1e red.)

O_3 ($E^0(O_3/O_2)$ = +2.08 V_{NHE}; 2e red.)

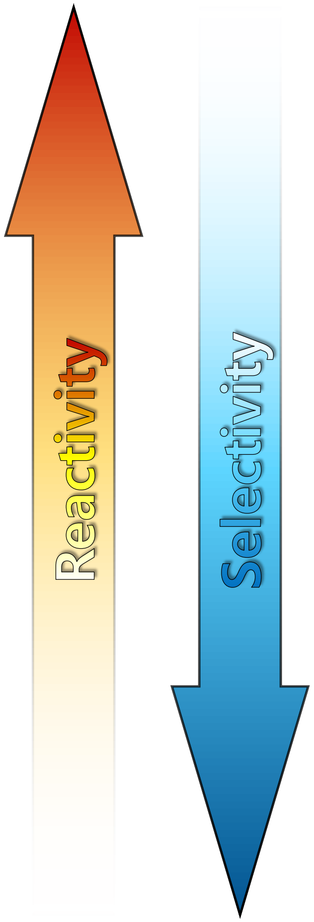
H_2O_2 ($E^0(H_2O_2/2H_2O)$ = +1.776 V_{NHE}; 2e red.)

Fe(VI) (E^0(Fe(VI)/Fe(III)) = +2.20 – 0.7 V_{NHE}; 3e red.)

Cl_2 ($E^0(Cl_2/2Cl^-)$+1.48 – 0.84 V_{NHE}; 2e red.)

ClO_2 ($E^0(ClO_2/ClO_2^-)$ = +1.04 V_{NHE}; 1e red.)

O_2 ($E^0(O_2/2H_2O)$ = +0.695 V_{NHE}: 2e red.)



Reactions of OH Radical

√ Reactivity of $^{\bullet}OH$

- Very reactive oxidant, $E^{o}(^{\bullet}OH/H_2O) = 2.8\ V_{NHE}$
- Very fast reactions with almost all of organic compounds

  $k = 10^{8} \sim 10^{10}\ M^{-1}\ s^{-1}$
- Very low steady-state concentration in natural water

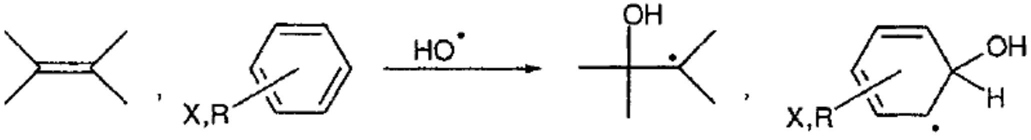
  $[^{\bullet}OH]_{ss} = 10^{-16} \sim 10^{-12}\ M$

√ Reaction mechanism of $^{\bullet}OH$

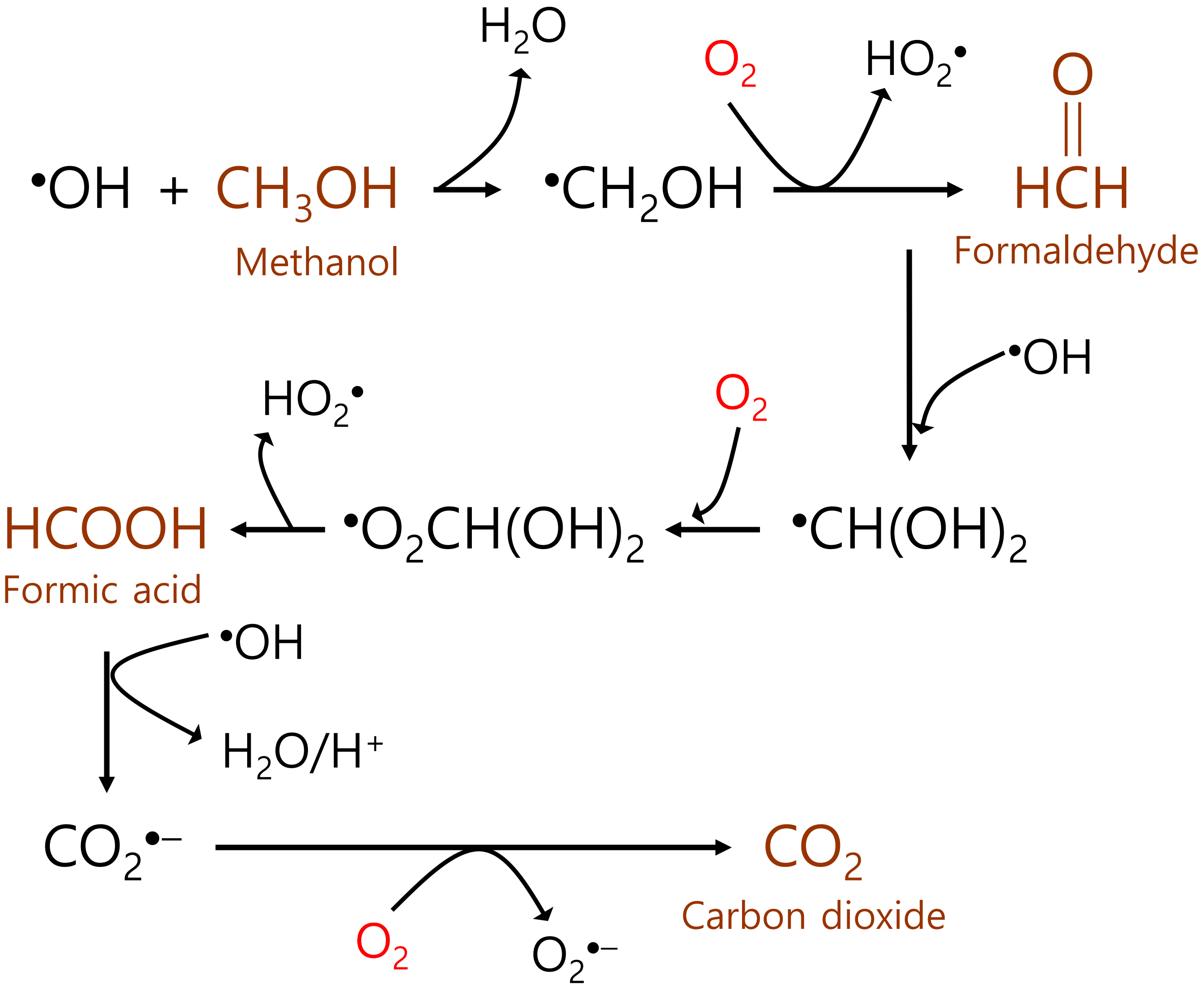
- H-Abstraction
- e^{-}-Abstraction
- Addition

$$R-H \xrightarrow{HO^{\bullet}} R^{\bullet} + H_2O$$

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+}$$



Oxidation of Methanol Initiated by •OH



$${}^{\bullet}OH + CH_3OH \xrightarrow{H_2O} {}^{\bullet}CH_2OH \xrightarrow{O_2 \qquad HO_2^{\bullet}} H\overset{\overset{O}{\|}}{C}H$$

Methanol

Formaldehyde

$$H\overset{\overset{O}{\|}}{C}H \xrightarrow{{}^{\bullet}OH} {}^{\bullet}CH(OH)_2 \xrightarrow{O_2} {}^{\bullet}O_2CH(OH)_2 \xrightarrow{HO_2^{\bullet}} HCOOH$$

Formic acid

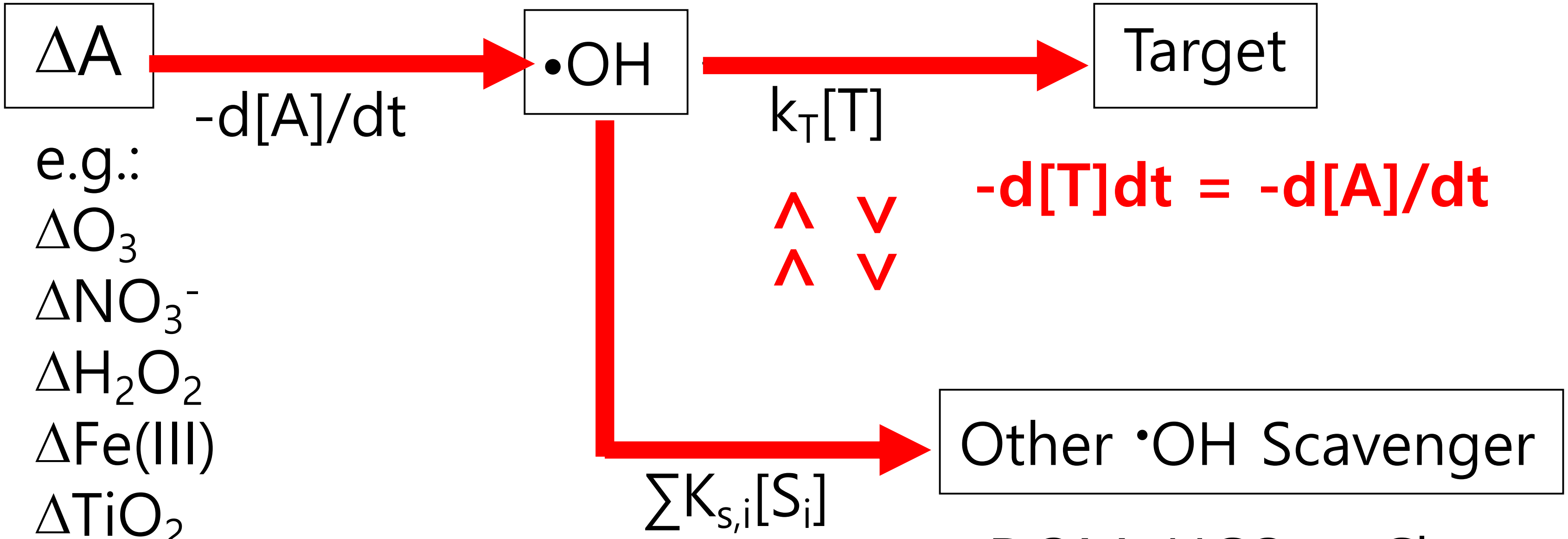
$$HCOOH \xrightarrow[H_2O/H^+]{{}^{\bullet}OH} CO_2^{\bullet -} \xrightarrow[O_2 \qquad O_2^{\bullet -}]{} CO_2$$

Carbon dioxide

Key Parameters in AOP

Rate and Yield for •OH

Distribution of •OH



ΔA

$-d[A]/dt$

•OH

$k_T[T]$

Target

$-d[T]dt = -d[A]/dt$

∧ ∨
∧ ∨

e.g.:
ΔO_3
ΔNO_3^-
ΔH_2O_2
ΔFe(III)
ΔTiO_2

$\sum K_{s,i}[S_i]$

Other $^{\cdot}$OH Scavenger

DOM, HCO_3^- , Cl^-
•OH precursors

$$-d[T]dt = k_T[T][\bullet OH]_{ss}$$

$$([\bullet OH]_{ss} = -(d[A]/dt) /(\sum K_{s,i}[S_i])$$

$$= -k_T \cdot (d[A]/dt)/(\sum K_{s,i}[S_i]) \cdot [T]$$

Classifications of AOPs

Thermal processes:

Ozonation

Conventional Fenton process

Electrochemical processes:

Direct electrolysis

Electro-Fenton

Photochemical process:

VUV

UV/TiO_2

UV/H_2O_2

Photo-Fenton

Direct H_2O dissociation:

VUV

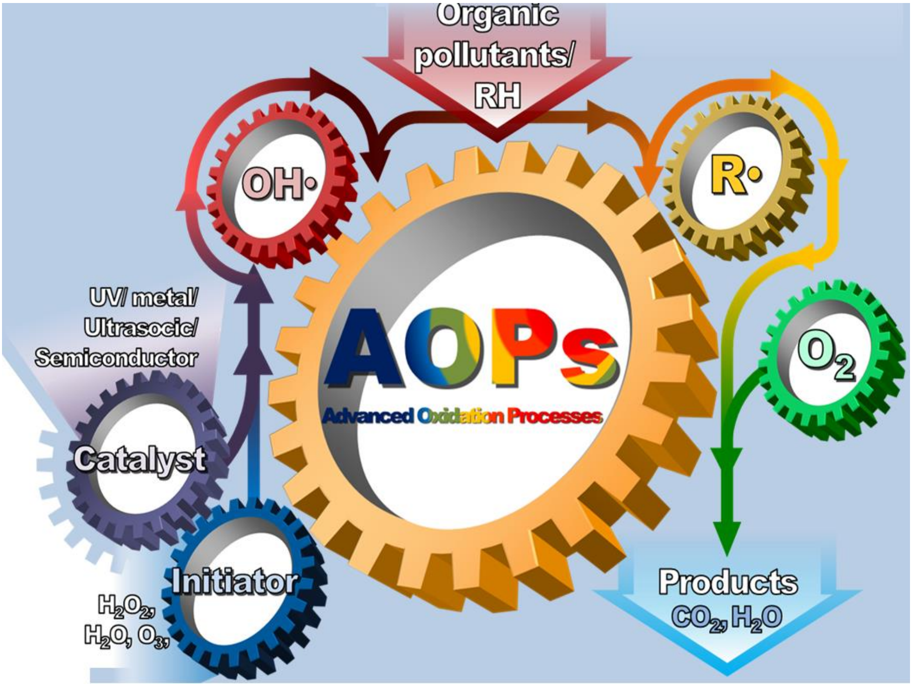
γ-radiolysis

Electron beam

Ultrasound

High-voltage discharge

Applications of AOPs



1. Drinking water treatment
   (e.g., ozonation, UV/H_2O_2)

2. Wastewater treatment
   (e.g., Fenton processes, ozonation)

3. Groundwater remediation
   (e.g., Fenton process, ozonation, inorganic oxidants w/ or w/o catalysts)

4. Disinfection and biofilm control
   (e.g., ozonation, photocatalysts)

5. Production of ultrapure water
   (e.g., VUV)

6. Sludge pretreatment

Qualitative Analysis of OH Radical

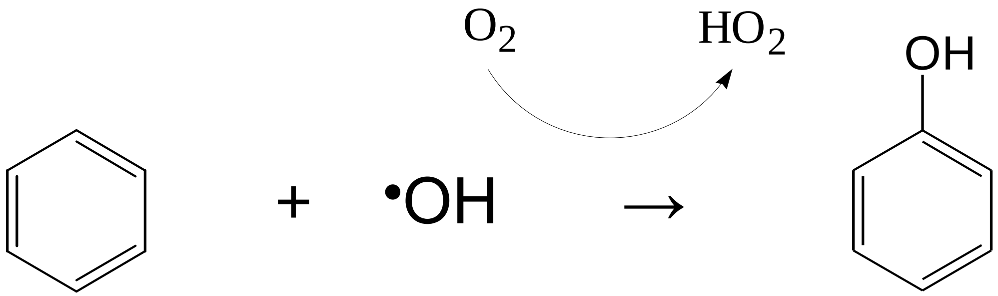
1. Analysis of oxidized product

2. Electron spin resonance (ESR) spectroscopy

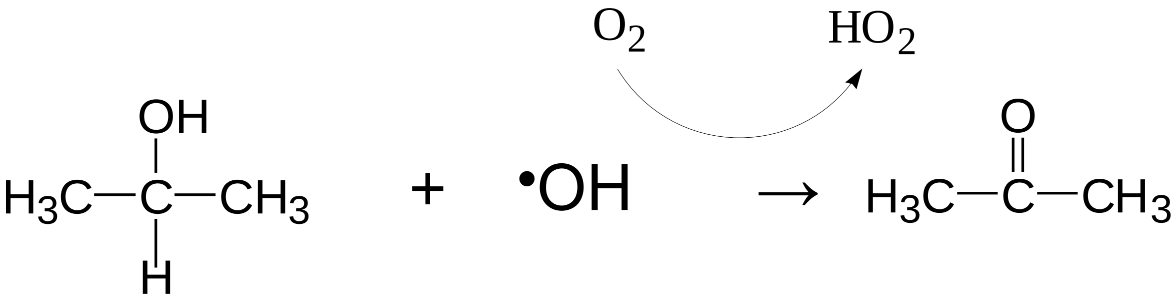
Analysis of Oxidized Products

Use of probe compounds, of which oxidized products by $^\bullet$OH are well-known

e.g.



benzene phenol



$$H_3C-CH(OH)-CH_3 + {}^\bullet OH \xrightarrow{O_2 \;\to\; HO_2} H_3C-C(=O)-CH_3$$

2-propanol Acetone

Electron spin resonance (ESR) spectroscopy

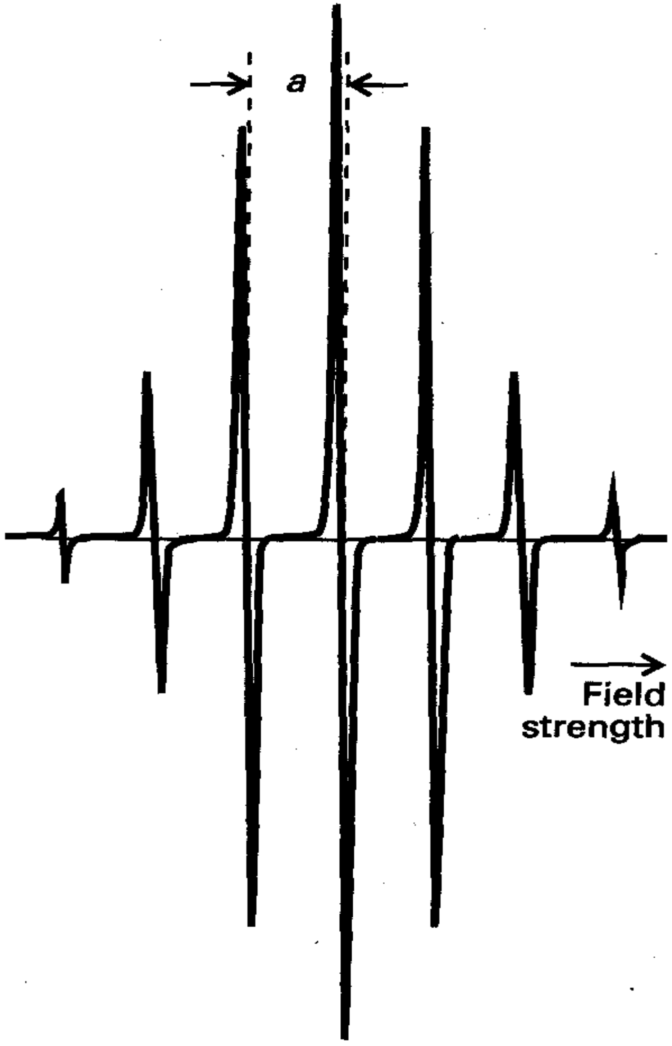
What is ESR (Electron Spin Resonance spectroscopy)

Or EPR (Electron Paramagnetic Resonance spectroscopy)

(전자스핀 공명 분광법)

- Spectroscopy based on the magnetic properties of electron spin movement of free radicals
- Free radical: any atoms or chemical species that possesses one or more unpaired electrons.
- The energy levels of free radicals split under the magnetic field.
- Certain wavelengths of microwave corresponding to these energy gaps can be absorbed to present signals.
- Electron Paramagnetic Resonance spectroscopy (EPR)
- Similar mechanism to NMR
- Information obtained from ESR data : g-value, hyperfine constant (hfc), signal intensity
- Identification of unknown radicals by the comparison with the signal database of standard radical species

Signal Output



g-value

The ESR spectrum of the benzene radical anion ($C_6H_6^{\bullet -}$)

a: the hyperfine splitting of the spectrum

g-value : the center of the spectrum

Theory

- **Energy separation in a magnetic field**

- Energy levels of an electron spin in a magnetic field B

$$E_{ms} = g_e \mu_b m_s B, \quad m_s = \pm 1/2$$

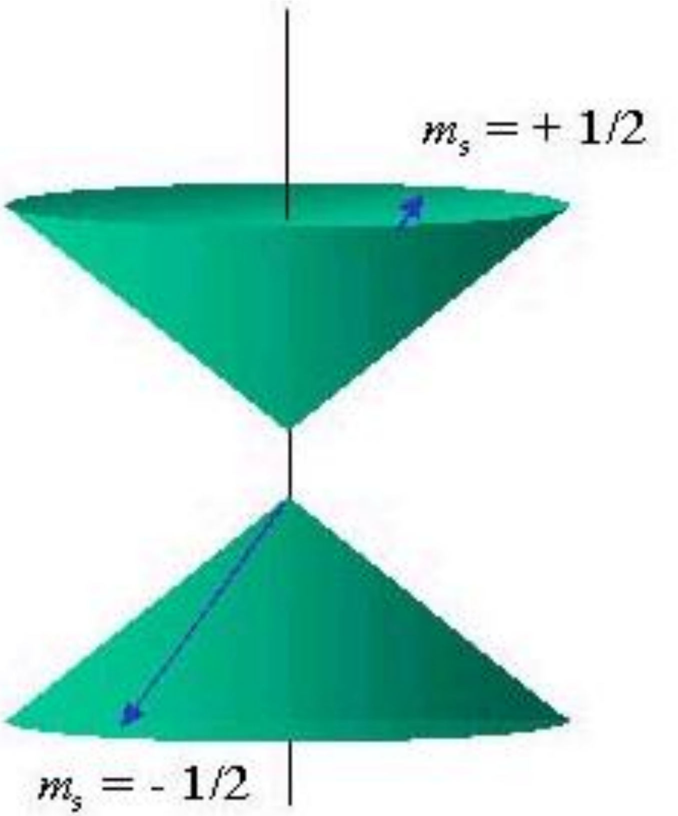
g_e : g-value of electron (= 2.002)

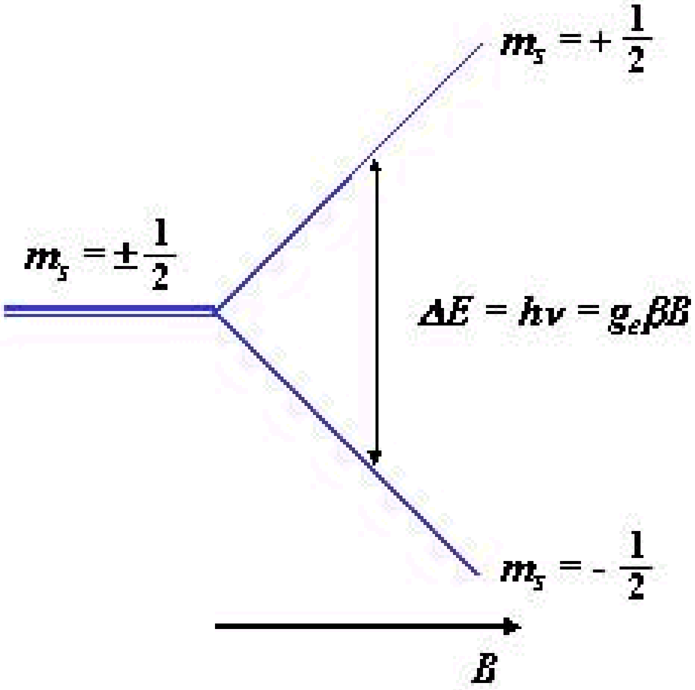
μ_B : Bohr magneton (9.274×10^{-24} J/T)
m_s : spin magnetic quantum number

- Separation of the levels

$$\Delta E = g_e \mu_b B$$

Theory





Electron’s Electromagnetic angular momentum

Zeeman splitting in the magnetic field

Theory

- **The g-value**

- Energy levels of an electron spin in a **local** magnetic field

$$\Delta E = h\nu = g_e\mu_B B_{log} = g_e\mu_B(1-\sigma)B$$

$$= g\ \mu_B B \qquad (\text{ where } g = (1-\sigma)g_e\ )$$

g : g-value of the specific radical or complex

- g-values : Many organic radicals $\approx$ 2.002 (g_e)
  Inorganic radicals 1.9 ~ 2.1
  d-metal complexes 0 ~ 4

Theory

- **Hyperfine structure**

- Most important feature of ESR spectra

- Splitting of individual resonance lines into component

- The source of the hyperfine structure in ESR is the magnetic interaction between the electron spin and the magnetic dipole moments of the nuclei present in the radical

Theory

The effect of nuclear spin

- Effect of **a single H nucleus (I=1/2)** located somewhere in a radical

$$B_{loc} = B + a\,m_I, \qquad m_I = \pm 1/2$$

m_I : spin magnetic quantum number of nucleus

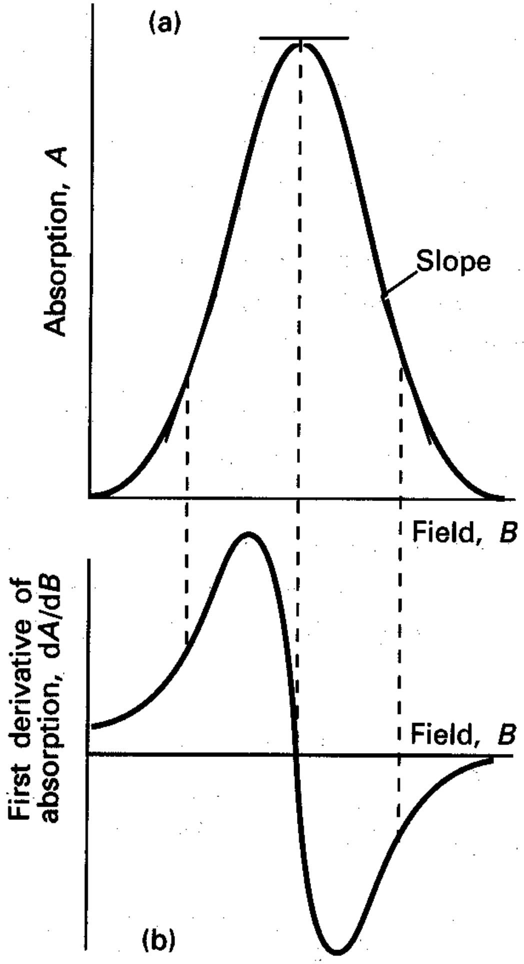
a : hyperfine coupling constant

$$h\nu = g_e\mu_B B_{log} = g_e\mu_B(B \pm 1/2\,a) \quad \text{two peaks}$$

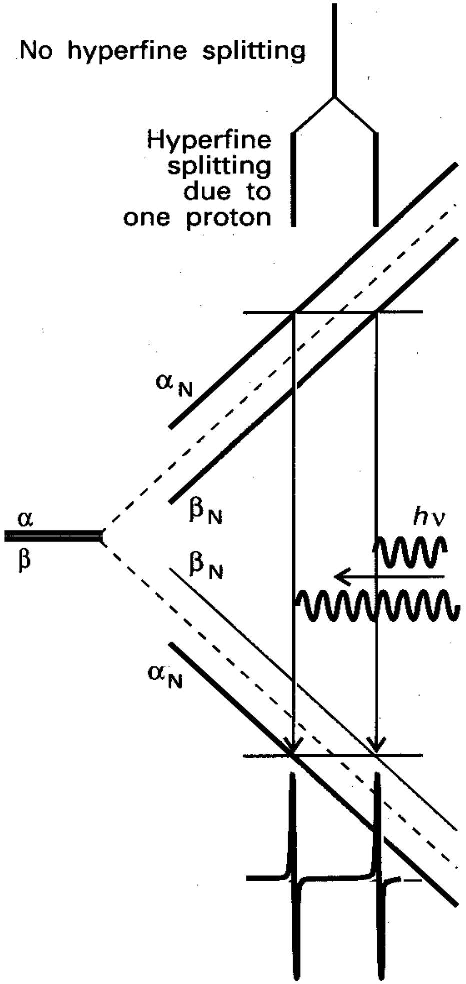
- In the case of **a single N nucleus (I=1)**

$$m_I = 0, \pm 1 \qquad \Rightarrow \qquad \text{three peaks splitting}$$

Interpretation of Output Signal



Signal is the first derivative of the absorption intensity



Hyperfine splitting

Analysis of Free Radicals by ESR

- The minimum concentration of radicals for the ESR analysis : 10^{-6} M

- Methods for analyzing short-lived free radicals

(1) Rapid mixing

(2) Rapid Freezing

(3) **Spin-trap method:**
Formation of more stable radicals by reactions between spin-trap agents and radicals

Analysis of Free Radicals by ESR with Spin Trap Agents

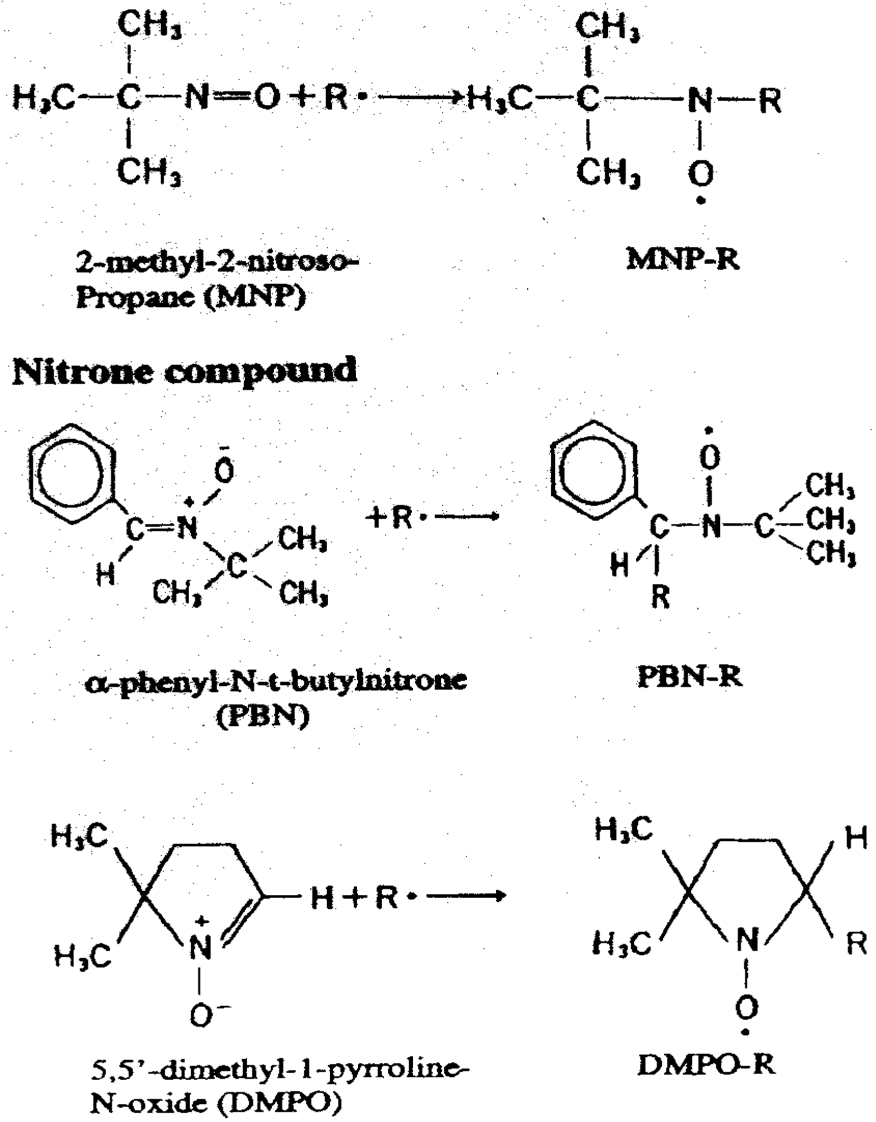
- The reaction of the free radical and the spin-trap agent produces a specific spin adduct (a more stable radical species), of which signal can be readily measured by ESR.

- Developed by Janzen and Blackburn (1969)

- Buettner's review paper summarizes various parameters of spin adducts

Buettner, G. R., "Spin trapping ; ESR parameters of spin adducts", *Free Rad. Biol. Med*., 1987, 3, 259-303.

Analysis of Free Radicals by ESR with Spin Trap Agents



2-methyl-2-nitroso-Propane (MNP)

MNP-R

Nitrone compound

α-phenyl-N-t-butylnitrone (PBN)

PBN-R

5,5'-dimethyl-1-pyrroline-N-oxide (DMPO)

DMPO-R

- Spin-trapping agents

- Addition of a free radical to an unsaturated bond

- Leading to a longer lived new radical (nitroxyl free radical)

⇐ Spin-trap agents and their radical adducts

DMPO Spin-Trapping

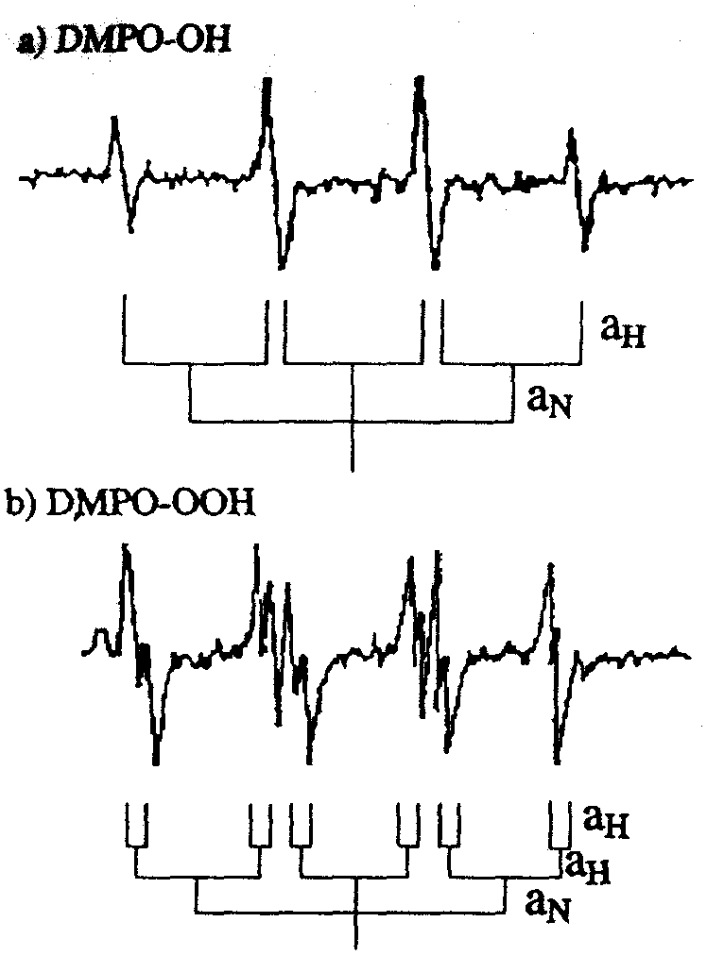
- DMPO : soluble in water, the only spin-trap agent seperating $\cdot OH$ and $HO_2\cdot$

- Useful for analyzing oxygen-based radicals

Table: ESR parameters of DMPO spin adducts

adduct	solvent	lines	a_N	a_H	Others
• H	Water	9	16.6	22.5(2)	
• OH	Water	4	15.0	15.0	
• OOH	Water	12	14.2	11.3	0.13(H)
• CH_3	Water	6	16.3	23.2	
• Cl	Benzene	12	14.3	11.7	

DMPO Spin-Trapping



Typical spectra of DMPO-adducts

- DMPO-OH
  4 peaks of intensity rate = 1:2:2:1

- DMPO-OOH
  12 peaks of same intensity

DMPO Spin-Trapping

- An excess amount of DMPO should be employed to catch all the radicals generated in the system.

- A quick analysis is needed because the DMPO adduct is still unstable.

  - Spin adducts are also radicals, which means they are still unstable.
    (= Accurate quantification of radical species is always hard!)

  - The lifetime of spin adducts depends on the species and conditions
    e.g., The half-life of DMPO-H is 1 min at 25^{o}C.
    The half-life of DMPO-OH is 10~20 min at 25^{o}C.

Kinetics of DMPO Spin Adduct

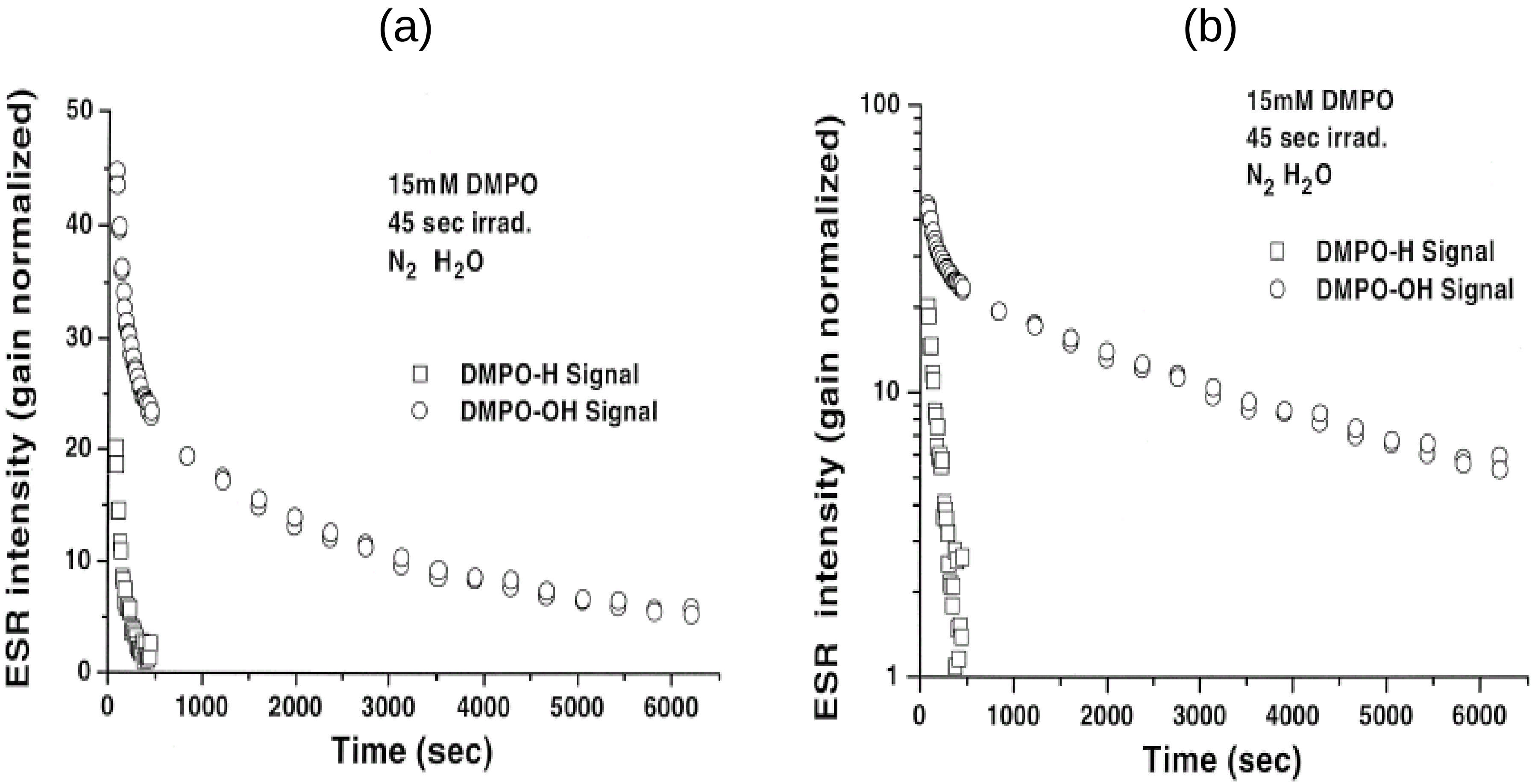
- Kinetic information (rate constants of spin adduct formation and decay) is essential for quantitative studies

- Decay constants of DMPO-OH

DMPO-OH + DMPO-H → $k = 2.44 \times 10^2$ M^{-1} s^{-1}
DMPO-OH + DMPO-OH → $k = 11$ M^{-1} s^{-1}

Hydroxyl radical scavenging efficiency
- 35 % using cobalt-60 γ ray (Carmichael *et al.*, 1984)
- 33 % using H_2O_2 photolysis (Sun *et al.*, 1996)
- 94 % at 100 μs after the electron pulse using cobalt-60 γ ray
  44 % at 15 s after the electron pulse using cobalt-60 γ ray
  (Madden and Taniguchi, 2001)

Kinetics of DMPO Spin Adduct



Linear (a) and semilogarithmic (b) kinetic plot of the spectral intensity of the DMPO-H and the DMPO-OH

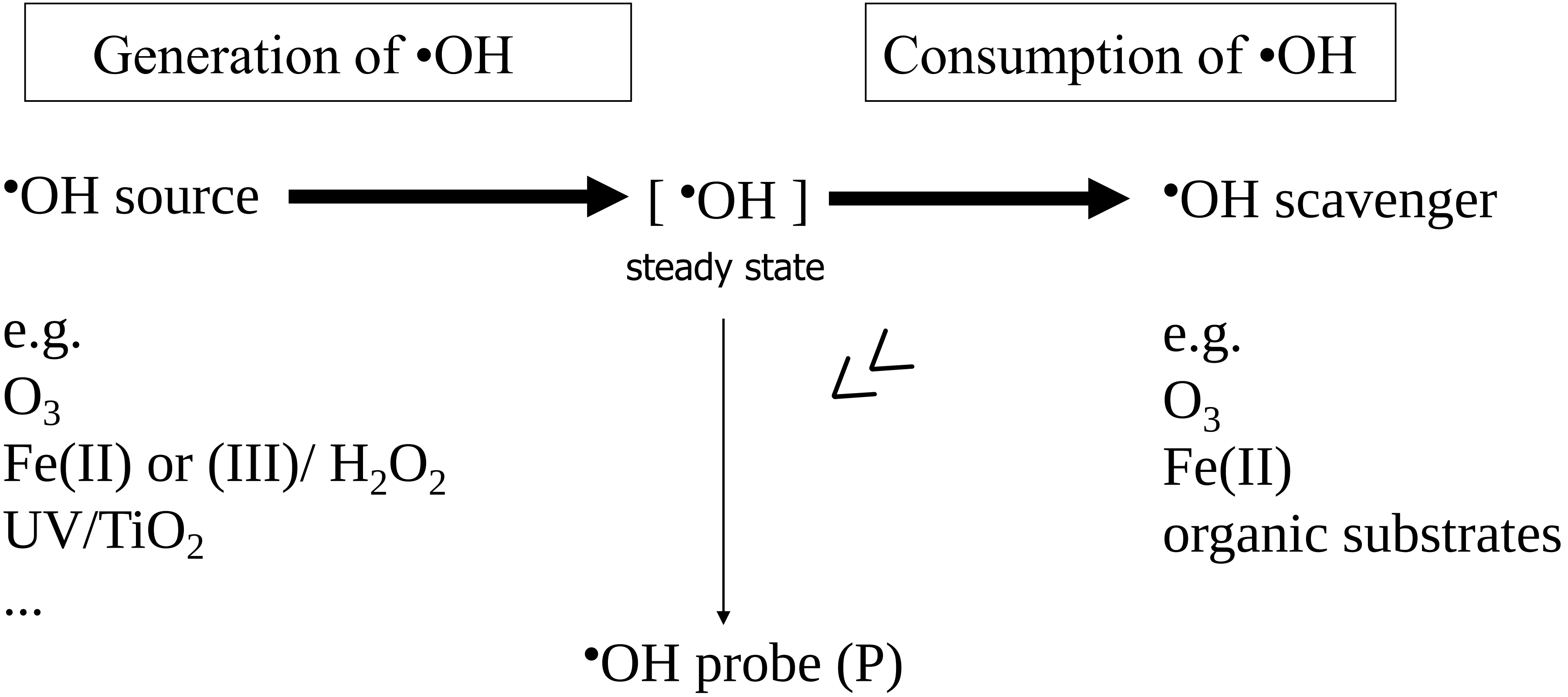
Quantitative Analysis of OH Radical

Kinetic methods for quantitative analysis of $^{\bullet}$OH in water

1. Analysis of steady-state $^{\bullet}$OH concentration
2. Analysis of $^{\bullet}$OH formation rate

Analysis of Steady-State •OH Concentration

- **Use of a low concentration •OH probe compound**



Generation of •OH

Consumption of •OH

•OH source → [•OH] → •OH scavenger

steady state

e.g.
O_3
Fe(II) or (III)/ H_2O_2
UV/TiO_2
...

e.g.
O_3
Fe(II)
organic substrates

•OH probe (P)

$$d[P]/dt = k_p[{}^\bullet OH]_{ss}[P]$$

Analysis of Steady-State •OH Concentration

- **Use of a low concentration •OH probe compound (procedure)**

1. Selection of a •OH probe compound
   - A compound of which rate constant with •OH is known
   - The rate constant with •OH should be high.
   - No significant reactions with other radical species in the system

2. Addition of a low concentration of the probe compound into the system

$$\mathbf{k[}{}^{\bullet}\mathrm{OH}][\mathrm{P}] \ll \Sigma k[{}^{\bullet}\mathrm{OH}][\text{other compounds in the system}]$$

note: •OH probe compound에 의한 •OH의 소멸량이 시스템 내 다른 화합물들에 의한 소멸량 보다 무시할 만큼 작아야 한다. 그렇지 않을 경우 probe compound 자체가 측정하려고 했던 정상상태 •OH농도에 영향을 미치게 된다.

Analysis of Steady-State •OH Concentration

3. [•OH]$_{ss}$ can be obtained by the first-order decay constant of the •OH probe compound ($k_{p,obs}$, s^{-1}) determined experimentally.

$$d[P]/dt = -k_{p,obs}[P]$$

$$= -k_p[{}^\bullet OH]_{ss}[P]$$

$$\Rightarrow \quad k_{obs,p}/k_p = [{}^\bullet OH]_{ss}$$

where k_p is the second order rate constant between the probe compound and •OH (M^{-1} s^{-1})

An Example of $[^{\bullet}OH]_{ss}$ Analysis

Example:

In order to measure the steady-state $^{\bullet}OH$ concentration in the Fenton process operated under the conditions of $[Fe(III)]_0 = 0.1$ mM, $[H_2O_2]_0 = 10$ mM, 30^{o}C, 2 μM of pCBA (*p*-chlorobenzoic acid) was added in the system and the variation of its concentration was observed with the reaction time.

Time (s)	[pCBA] (μM)
0	2
60	1.82
240	1.45
480	1.06
720	0.8
960	0.58

The time-concentration profile of pCBA is shown in the table.
Find the steady-state $^{\bullet}OH$ concentration.

(The second-order rate constant for the reaction of pCBA with $^{\bullet}OH$, k_{pCBA} is 5×10^{9} M^{-1} s^{-1})

An Example of $[^\bullet OH]_{ss}$ Analysis

Solution: First, we need to determine the first-order observed rate constant of the pCBA decomposition ($k_{pCBA,obs}$, s^{-1}).

$$d[pCBA]/dt = -k_{pCBA,obs}[pCBA]$$

$$\Rightarrow d[pCBA]/[pCBA] = -k_{pCBA,obs}\, dt$$

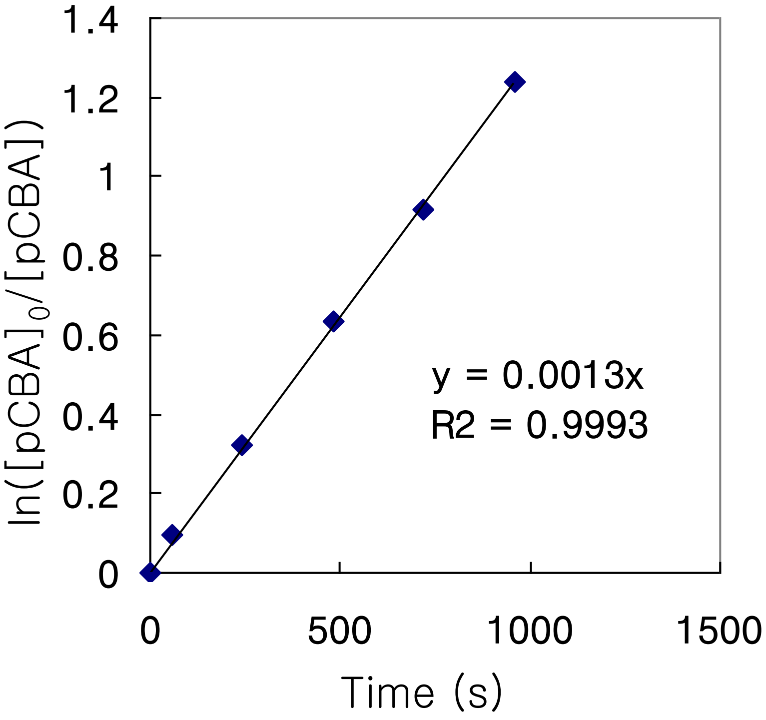
$$\Rightarrow \ln([pCBA]_0/[pCBA]) = k_{pCBA,obs}\, t$$

The $k_{pCBA,obs}$ value is the slope of the linear plot between $\ln([pCBA]_0/[pCBA])$ and t.

An Example of $[^{\bullet}OH]_{ss}$ Analysis

Time (s)	[pCBA] (μM)
0	2
60	1.82
240	1.45
480	1.06
720	0.8
960	0.58

$\ln([pCBA]_0/[pCBA])$
0
0.094
0.32
0.63
0.92
1.24



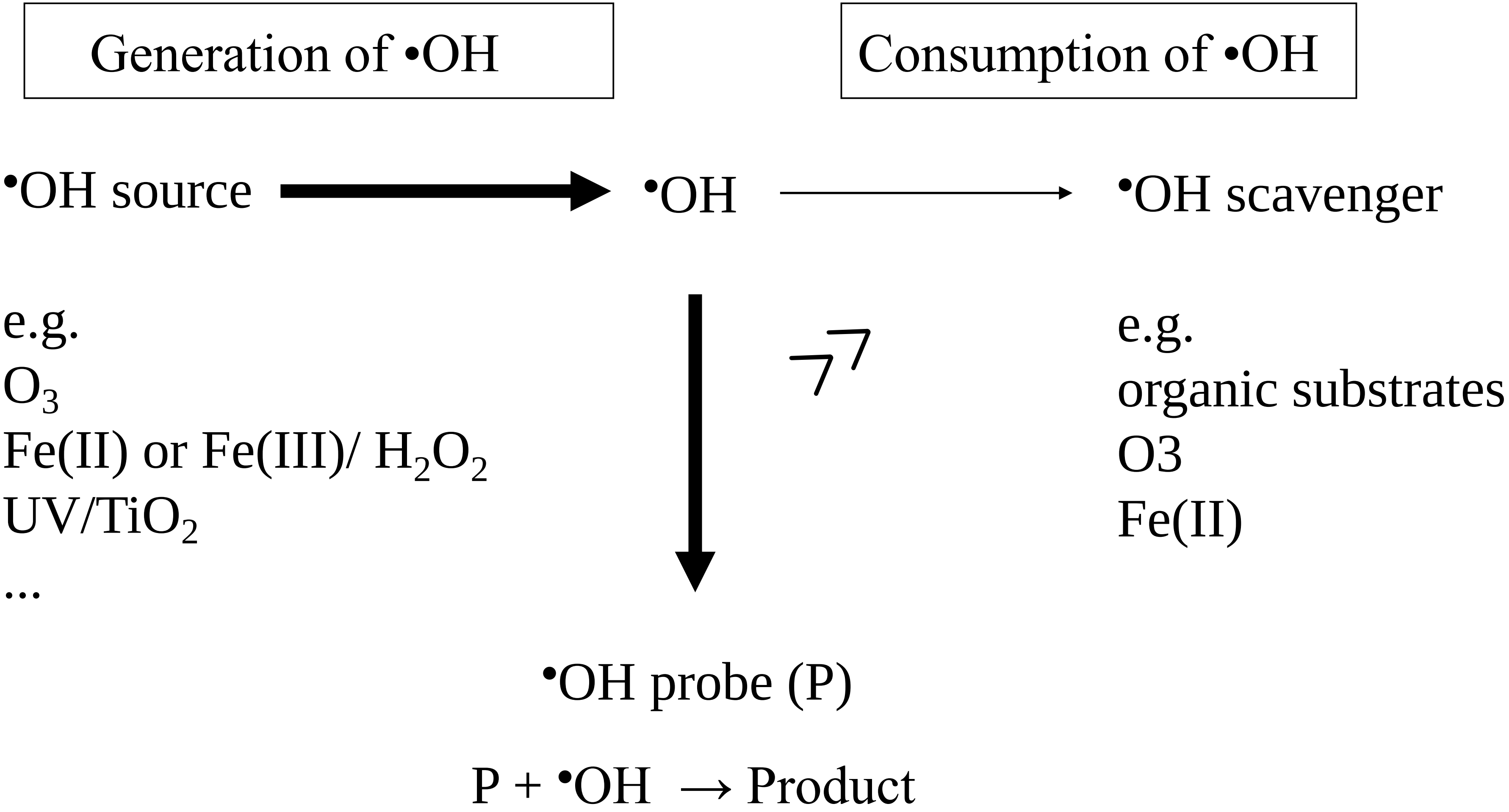
From the slope, $k_{pCBA,obs}$ **= 0.0013** $\mathbf{s^{-1}}$

Because $k_{pCBA,obs} = k_{pCBA}\,[^{\bullet}OH]_{ss}$, $\quad [^{\bullet}OH]_{ss} = k_{pCBA,obs} / k_{pCBA}$

$$= 0.0013\ s^{-1} / (5\times10^{9}\ M^{-1}\ s^{-1})$$
$$= 2.6\times10^{-13}\ M$$

Analysis of •OH Formation Rate

- **Use of excess •OH probe compound**



Generation of •OH

Consumption of •OH

•OH source → •OH → •OH scavenger

e.g.
O_3
Fe(II) or Fe(III)/ H_2O_2
UV/TiO_2
…

e.g.
organic substrates
O3
Fe(II)

•OH probe (P)

P + •OH → Product

Analysis of •OH Formation Rate

Use of excess •OH probe compound (procedure)

1. Selection of a •OH probe compound
   - A compound of which oxidized product by •OH is known
   - No significant reactions with other radical species in the system
     Or reactions that produce different products.

note: probe compound는 시스템내 다른 화학종들과 반응하지 않거나 반응하더라도
그 생성물이 달라야 한다.

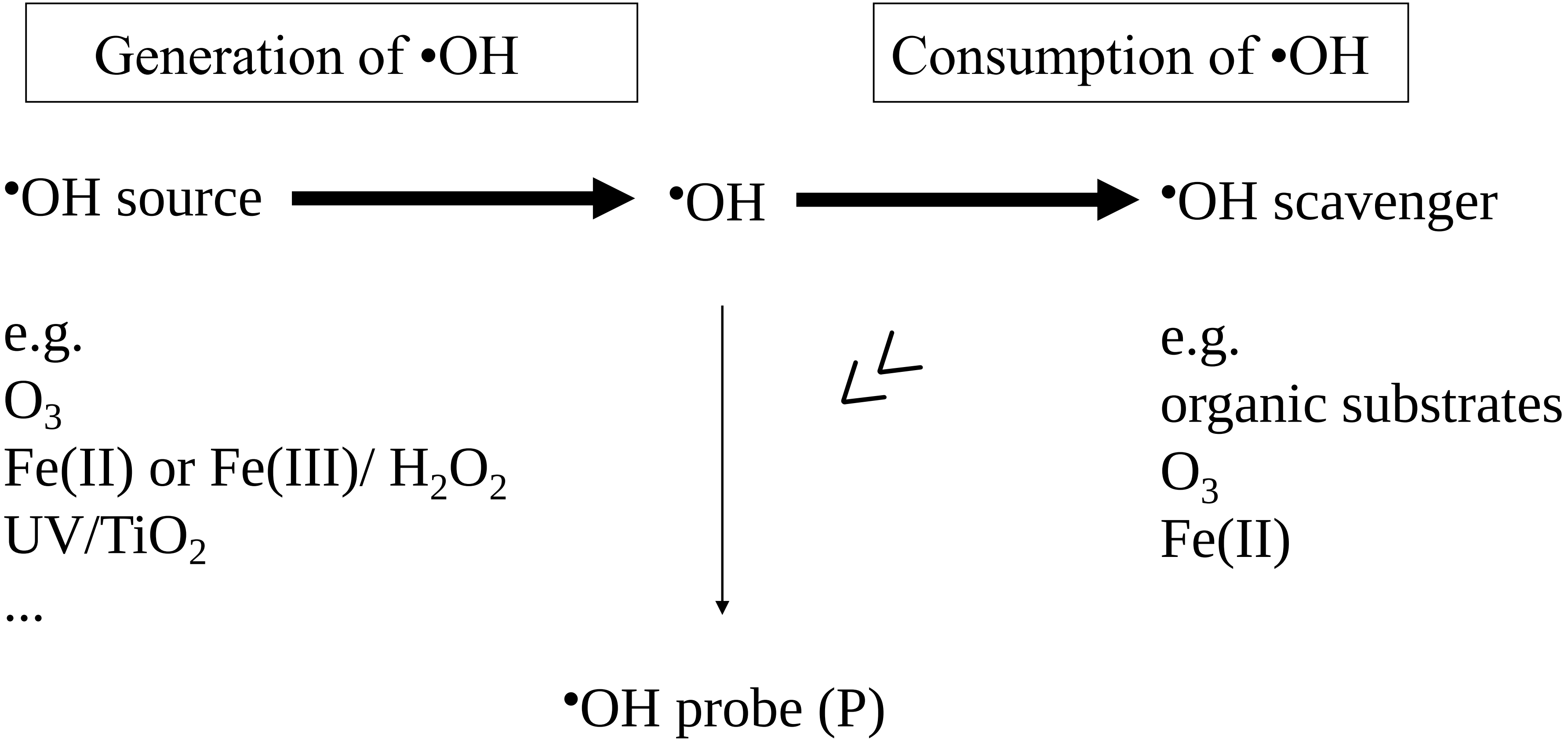
2. Input excess •OH probe compound into the system
   All the produced •OHs should react with the probe compound.

note: 생성되는 •OH들이 대부분 probe compound와 반응할 만큼의 농도를
가해야 한다.

•OH formation rate = the formation rate of the oxidized product

Analysis of •OH Formation Rate

- **Use of excess •OH scavenger and a low concentration of •OH probe compound**



Generation of •OH

Consumption of •OH

•OH source → •OH → •OH scavenger

e.g.
O_3
Fe(II) or Fe(III)/ H_2O_2
UV/TiO_2
…

e.g.
organic substrates
O_3
Fe(II)

•OH probe (P)

$$P + {}^{\bullet}OH \rightarrow \text{Product}$$

Analysis of •OH Formation Rate

- **Use of excess •OH scavenger and a low concentration of •OH probe compound (procedure)**

1. Selection of a •OH probe compound and a •OH scavenger
   - The oxidized products of the •OH scavenger should not interfere with the •OH probe compound.

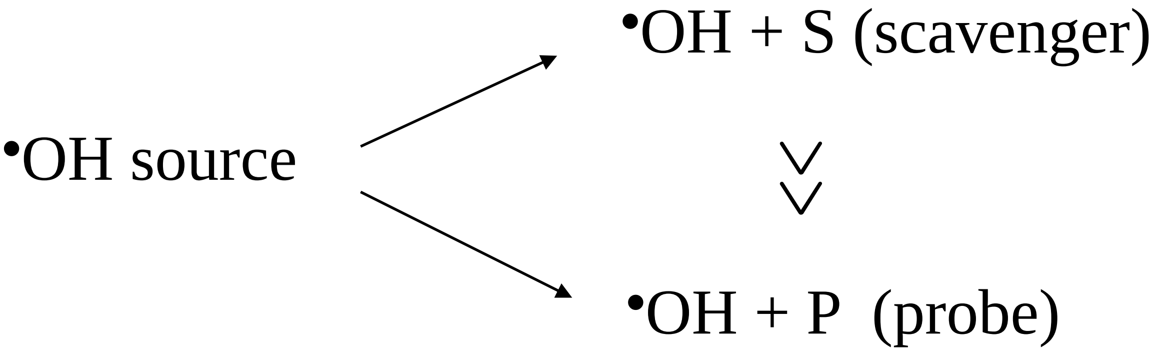
note: •OH scavenger의 경우 반응 생성물이 시스템에 영향을 주지 않는 화합물로 선정

2. Input excess •OH scavenger of a known concentration together with a low concentration of •OH probe compound

Note: •OH probe compound와 scavenger 농도조건:
생성된 •OH은 대부분 •OH scavenger와 반응하고 •OH probe compound와 •OH의 반응은 무시할 수 있는 농도를 가한다.

Analysis of •OH Formation Rate

3. The •OH formation rate can be obtained by the first-order decay constant of the •OH probe compound ($k_{p,obs}$, s^{-1}).



•OH source

•OH + S (scavenger)

$\vee$
$\vee$

•OH + P (probe)

•OH formation rate = r_{OH},

$$d[{}^{\bullet}OH]/dt = r_{OH} - (-d[S]/dt) = r_{OH} - (k_s[{}^{\bullet}OH]_{ss}[S]) \approx 0$$

$$\Rightarrow \quad r_{OH} = k_s[{}^{\bullet}OH]_{ss}[S]$$

On the other hand, $d[P]/dt = -k_{p,obs}[P] = -k_p[{}^{\bullet}OH]_{ss}[P]$

$$\Rightarrow \quad k_{obs,p}/k_p = [{}^{\bullet}OH]_{ss}$$

Therefore, $r_{OH} = k_s\, k_{p,obs}\, [S] / k_p$

Probe compound의 분해시간 동안 scavenger의 농도는 변하지 않는다고 가정

An Example of R_{OH} Analysis

Example: In order to measure the formation rate of $^{\bullet}OH$ in UV/H_2O_2 process, excess $^{\bullet}OH$ scavenger (t-BuOH 10 mM) and a small amount of $^{\bullet}OH$ probe compound (pCBA 2 μM) were added into the system, and the pCBA decomposition was observed.

Time (sec)	[pCBA] (μM)
0	2
240	1.80
480	1.61
980	1.30
1960	0.90

Find the formation rate of $^{\bullet}OH$.

(The second-order rate constant for the reaction of pCBA with $^{\bullet}OH$, k_p is 5×10^9 M^{-1} s^{-1}, and The second-order rate constant for the reaction of t-BuOH with $^{\bullet}OH$, k_s is 6.6×10^8 M^{-1} s^{-1})