Qualitative and Quantitative Analysis Of Radical Species in AOP

Qualitative Analysis of OH radical

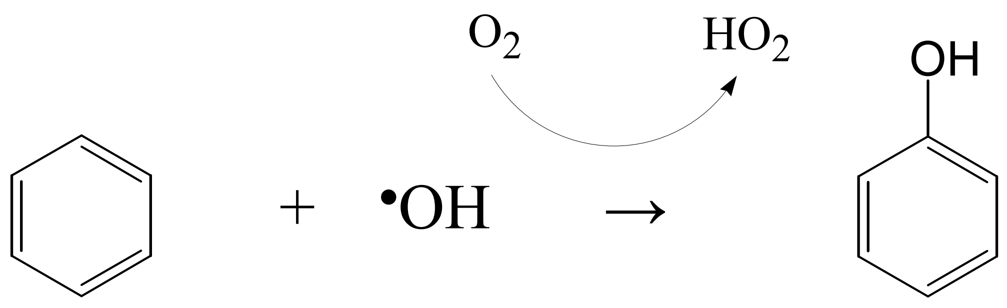
1. Analysis of diagnostic oxidized product

2. Electron Spin Resonance (ESR)

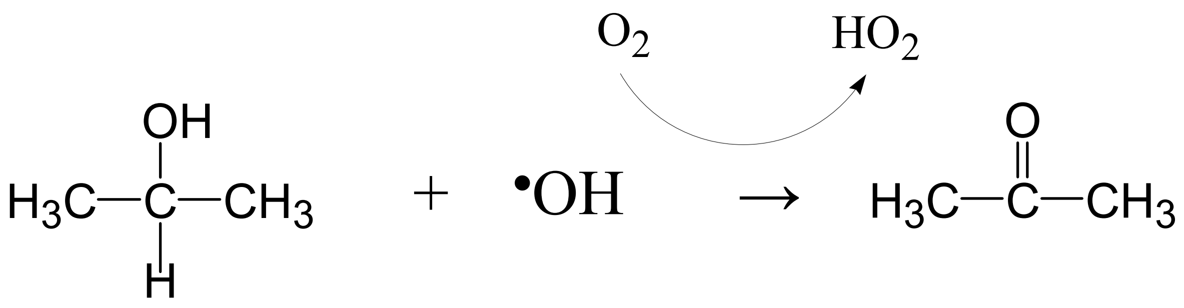
1. Analysis of diagnostic oxidized product

- Using the known reaction product with OH radical

e.g.



benzene phenol



2-propanol Acetone

2. Electron Spin Resonance (ESR)

ESR (Electron Spin Resonance Spectroscopy) ?

- Detecting free radical compounds using its magnetic property

- Free radical: any atom or group that possesses one or more unpaired electrons

- Electron paramagnetic resonance spectroscopy (EPR)

- Free radical located under magnetic field: Energy levels of an electron spin in a magnetic field is separated (Zeeman separation). As microwave irradiation is applied externally, the hyperfine structure of splitting is generated. 에너지 상태는 안전과 불안정으로 분열. 여기에 마이크로파를 조사하면 에너지를 흡수하여 전이

- Hyroxyl radical spin trapping (for OH radical)
- Comparison with reference information

Signal output of ESR

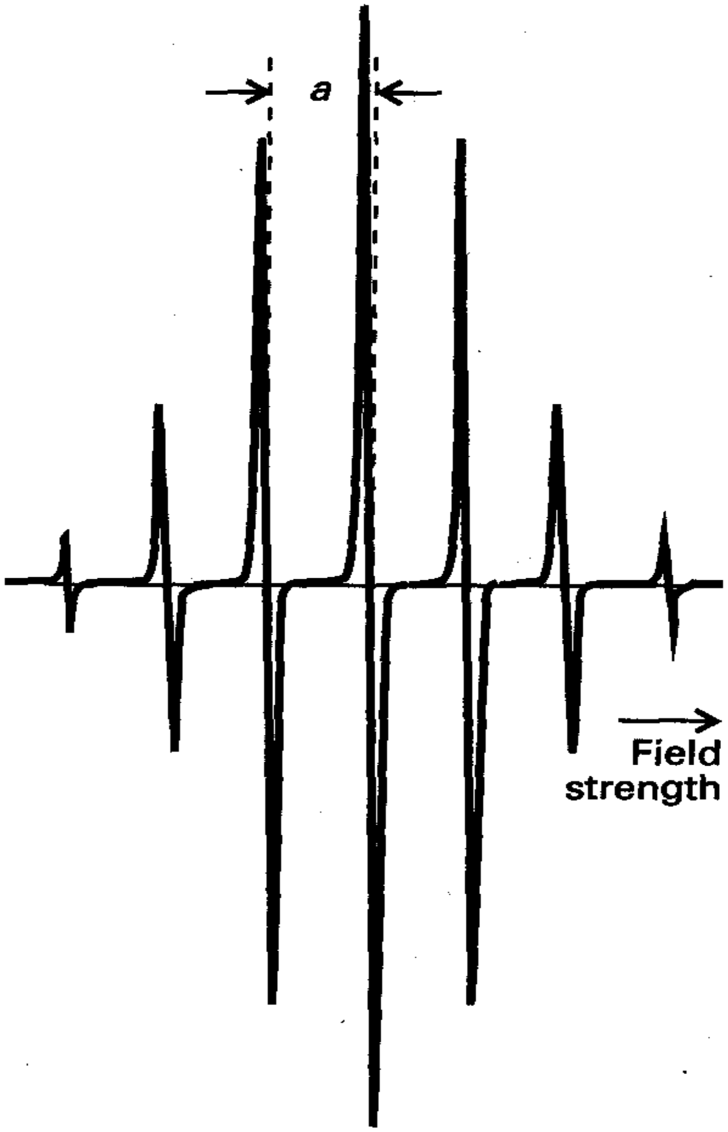


Fig. 1 The ESR spectrum of the benzen radical anion ($C_6H_6^-$) in fluid solution

g-value : the center of the spectrum

g-value of the specific radical or complex

a: the hyperfine splitting of the spectrum

splitted lines, signal intensity

Detecting free radiacl by ESR

- Minimal concentration of radical for ESR signal detection: 10^{-6} M

- Several approaches

(1) 신속 혼합법: detecting radical itself without any pretreatment,

~ difficult for kinetic study

(2) Freezing method: freezing radical before the analysis to slow down the signal reduction

~ difficult for accurate interpretation of signal

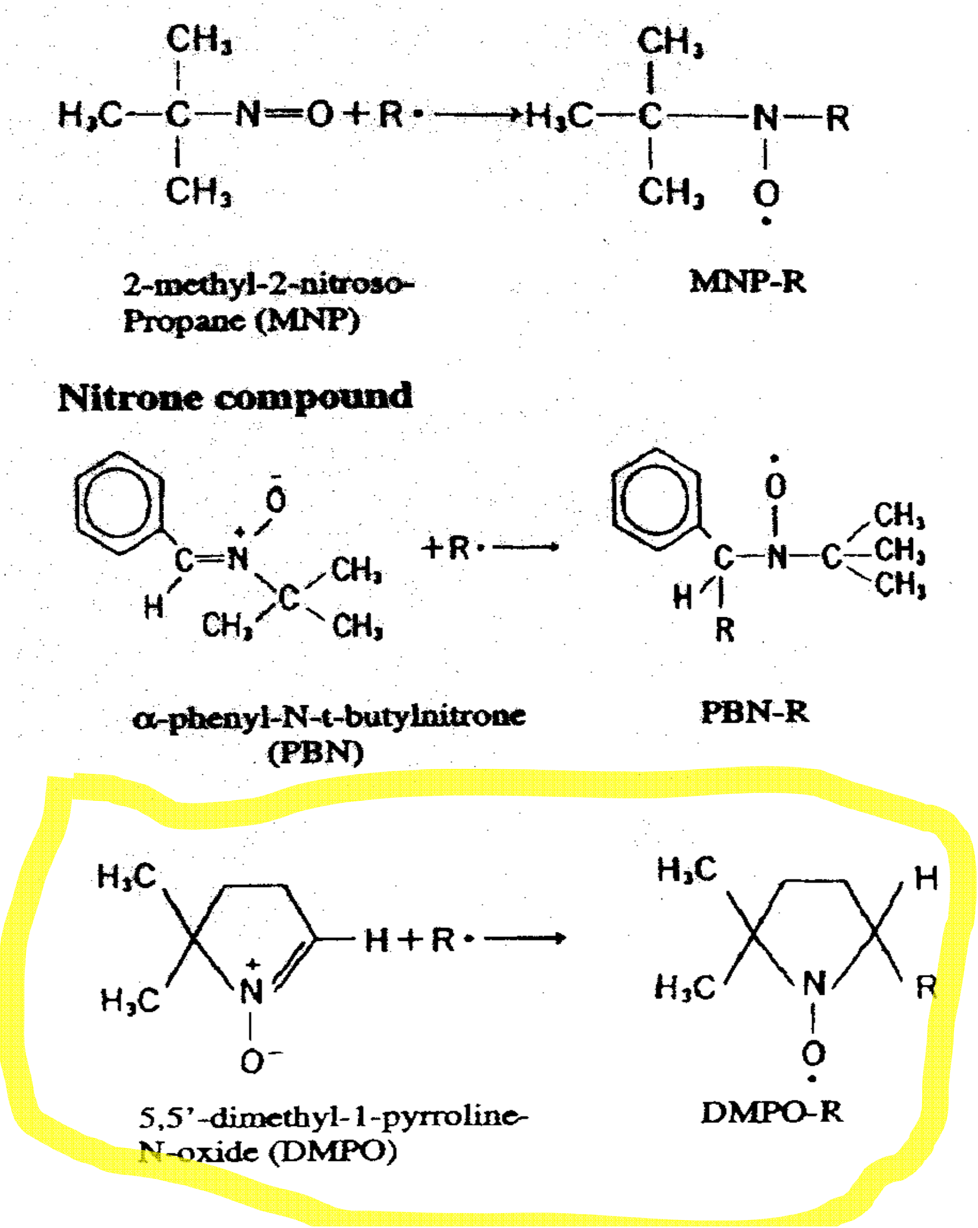
(3) **Spin-trap method:** Detecting the ESR signal of stable radical adduct which is the product between the radical of interest and the spin trapping agent

* Detecting the ESR signal of stable radical adduct which is the product between the radical of interest and the spin trapping agent

* Suggested by Janzen & Blackburn (1969)

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

Representative Spin−trapping agents



- Spin-trapping agents

  - addition of a free radical to an unsaturated bond

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

Fig. 6 Spin-trap agents and their radical adducts

DMPO spin−trapping 에 의한 radical 분석 (1)

- DMPO : a useful spin trapping agent for differentiating ·OH from HO_2·
  ($3.1 \times 10^9\ M^{-1}s^{-1}$)

- 산소중심 라디칼 측정에 유용

Table 1 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 에 의한 radical 분석 (2)

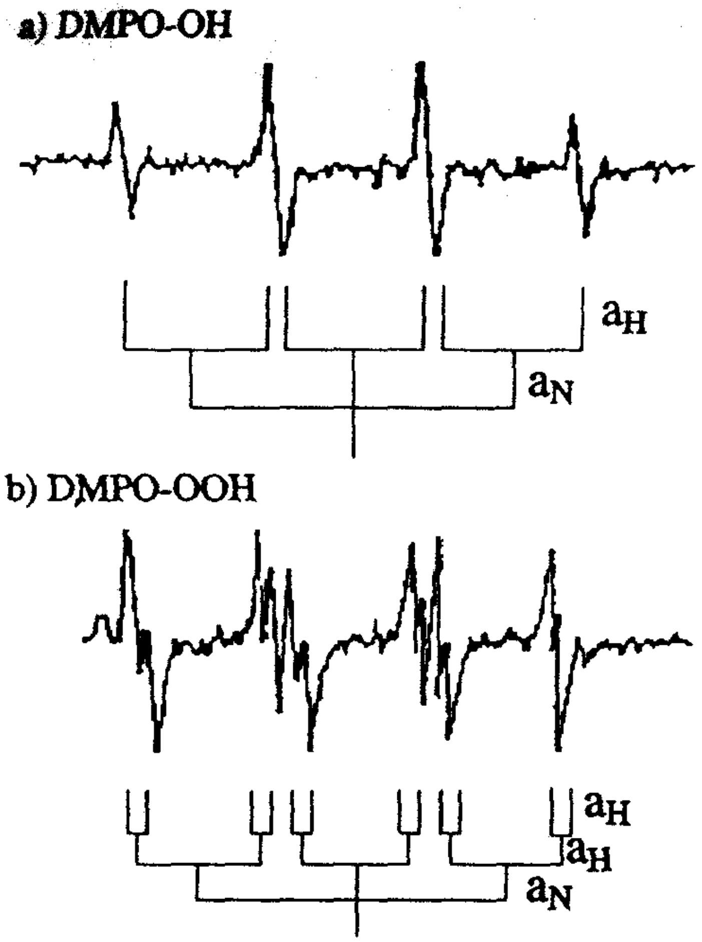


Fig. 7 Typical spectra of DMPO-adducts

- DMPO-OH
  4 peaks
  1:2:2:1 intensity
- DMPO-OOH
  12 peaks

ESR measurement using DMPO spin−trapping

- Excess scavenger (DMPO) is required

- Rapid determination for DMPO adduct (still unstable) is recommended

ex) $t_{1/2}$ (DMPO-OH) = 10~20 min

$t_{1/2}$ (DMPO-H) = 1 min (25^{o}C)

Kinetics of DMPO spin adduct (1)

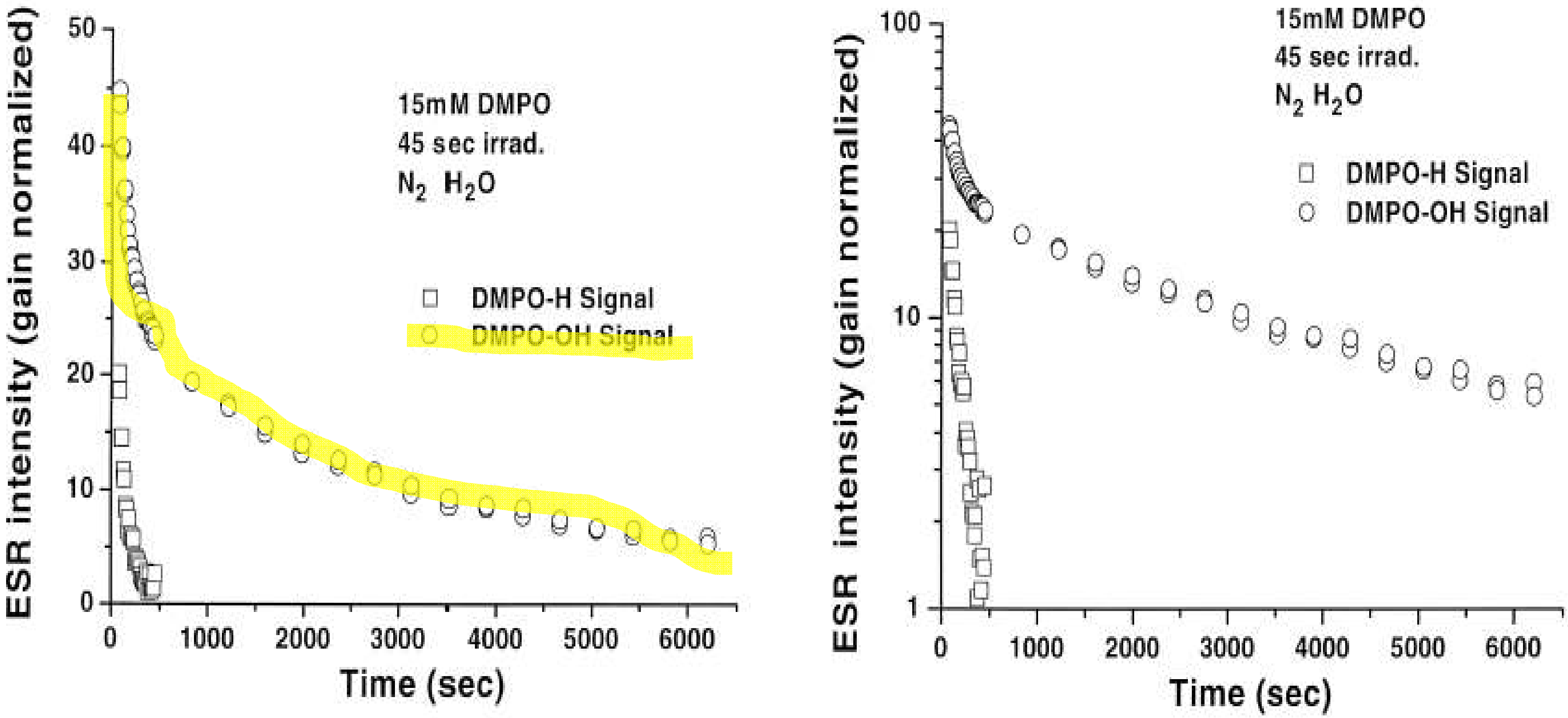
- Kinetic information (rate constants of spin adduct formation and decay) is essential for quantitative studies

- Decay constants of DMPO-OH

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

  DMPO-OH + DMPO-OH → $k = 11\ M^{-1}\ s^{-1}$

Kinetics of DMPO spin adduct (2)


(a)

(b)

Fig. 8 Linear (a) and semilogarithmic (b) kinetic plot of the spectral intensity of the DMPO-H and the DMPO-OH

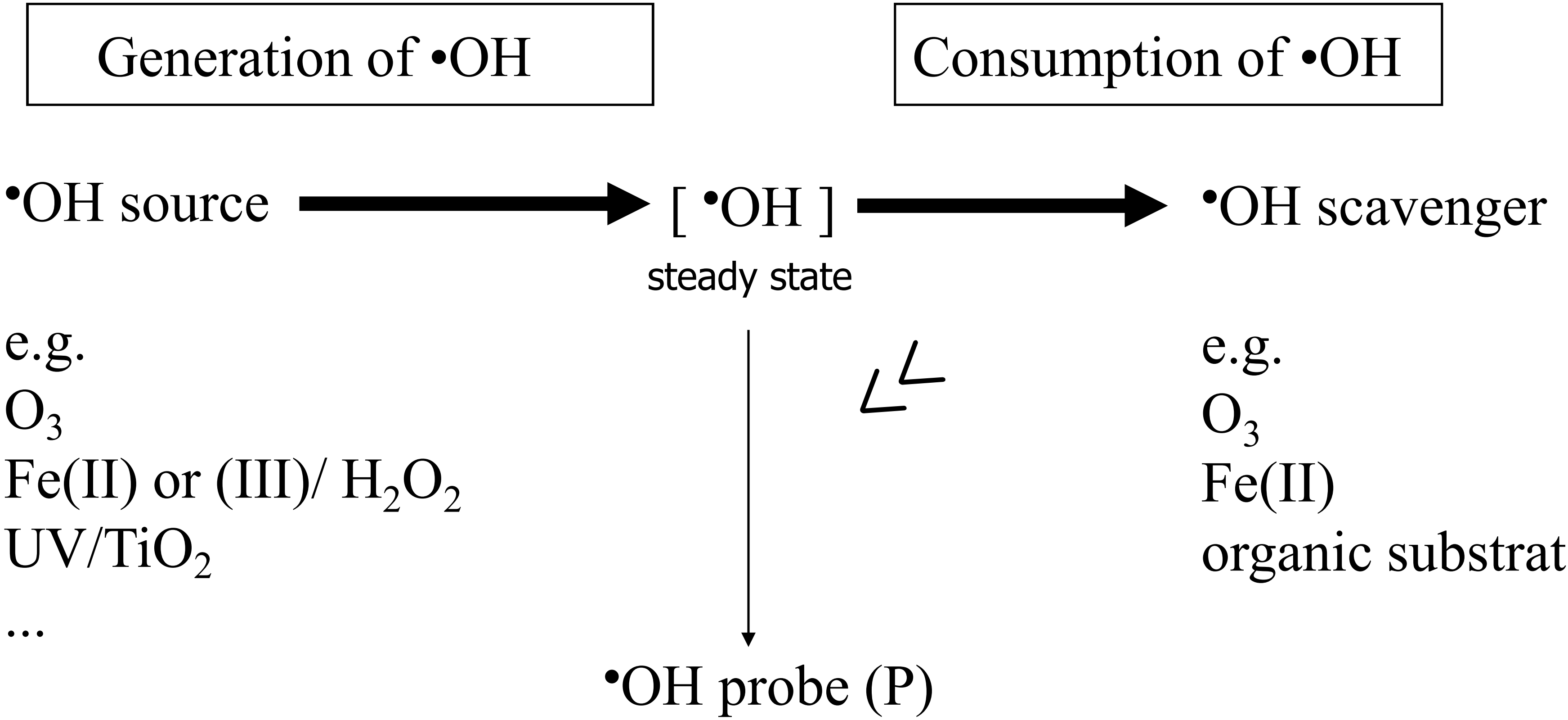
Kinetic Method for Quantitative Analysis of • OH in Aqueous Solution

1. Measurement of steady state •OH concentration

2. Formation rate of •OH

Detecting the steady state concentration of •OH

Trace amounts of •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)

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

Detecting the steady state concentration of •OH

1. The selection of •OH probe compound: the rate constant with •OH rapid and is known (the reactivity of this probe compound with other compounds should be inert or weak.
2. The use of trace amounts of the •OH probe compound; This •OH probe compound should not affect the level of •OH concentration in the system

3. Find out the $k_{p,obs}$ (s^{-1}) first and calculate $[\bullet OH]_{ss}$ from it.

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

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

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

k_p : the reaction constant of probe compound with ${}^\bullet OH$ (M^{-1} s^{-1})

Example : Measurement of $[{}^{\bullet}OH]_{ss}$

pCBA (*p*-chlorobenzoic acid, 2 μM) decreases in Fenton process ($[Fe(III)]_0 = 0.1$ mM, $[H_2O_2]_0 = 10$ mM, 30°C). Find out $[{}^{\bullet}OH]ss$.

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

k_p : the reaction constant of pCBA with ${}^{\bullet}OH$ ($M^{-1}\ s^{-1}$) ; $5\times10^9\ M^{-1}\ s^{-1}$

Solution: $[\bullet OH]_{ss}$

Find out the $k_{p,obs}$ (s^{-1}) first and calculate $[\bullet OH]_{ss}$ from it.

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

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

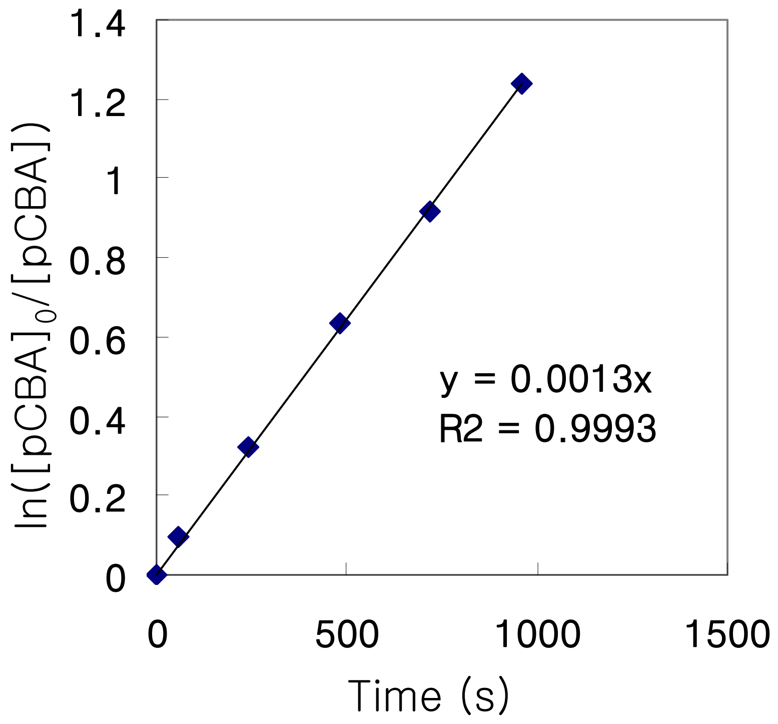
$$\Rightarrow \ln([pCBA]_0/[pCBA]) = k_{pCBA,obs}\,t$$

Form the linear relationship between $\ln([pCBA]_0/[pCBA])$ and time, find out $k_{pCBA,obs.}$

Solution: [•OH]ss

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



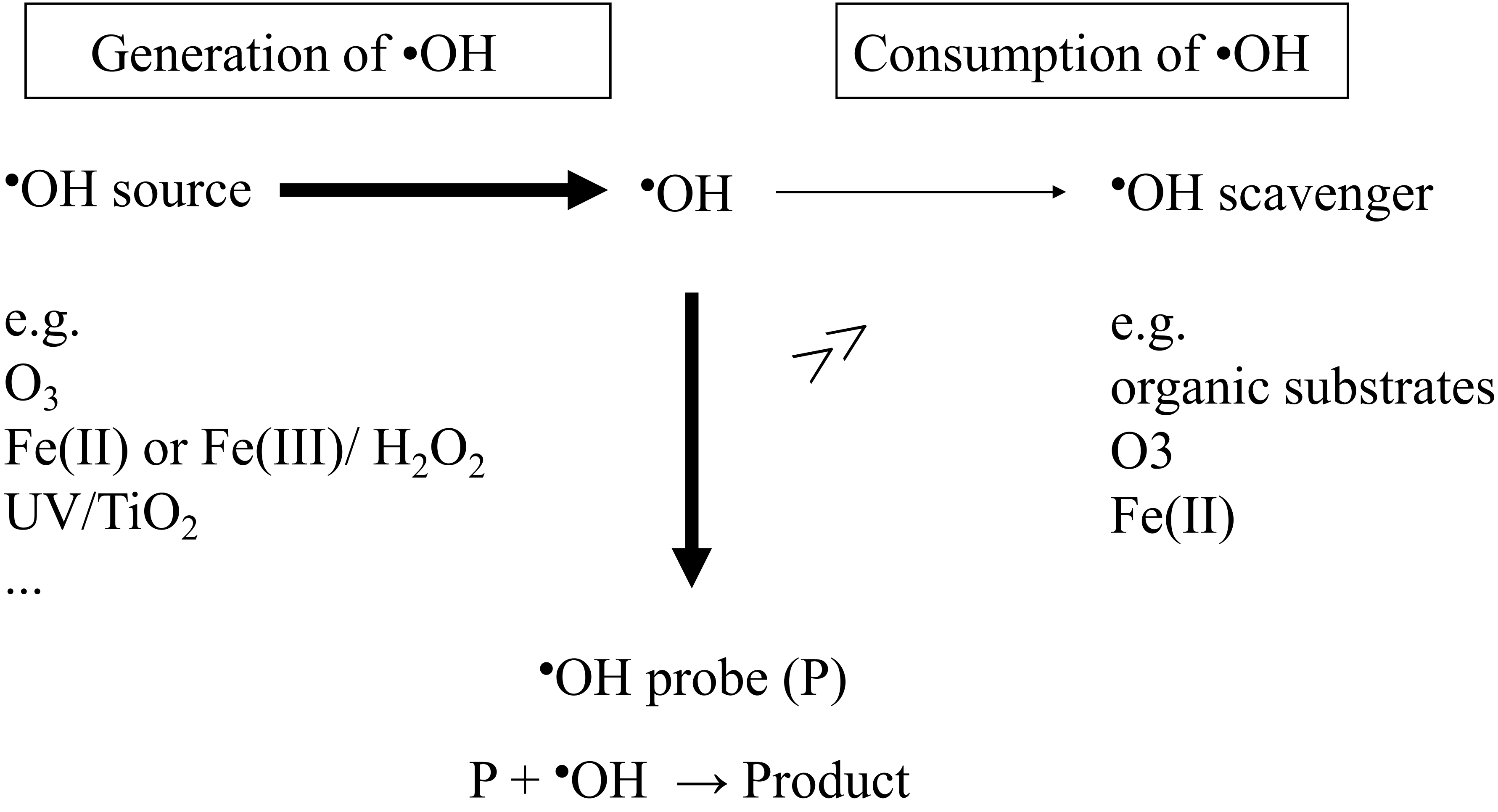
From slope, $k_{pCBA,obs} = 0.0013\ s^{-1}$

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

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

Measuring the formation rate of •OH

(1) Excess use 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
O3
Fe(II)

•OH probe (P)

P + •OH → Product

Detecting the •OH generation rate using excess •OH probe compound

1. The selection of •OH probe compound: the rate constant with •OH rapid and is known (the reactivity of this probe compound with other compounds should be inert or weak).

2. Excess •OH probe compound needs to be applied so that all the •OH generatged would be consumed with •OH probe compound

3. The generation rate of product A is equal to the generation rate of •OH

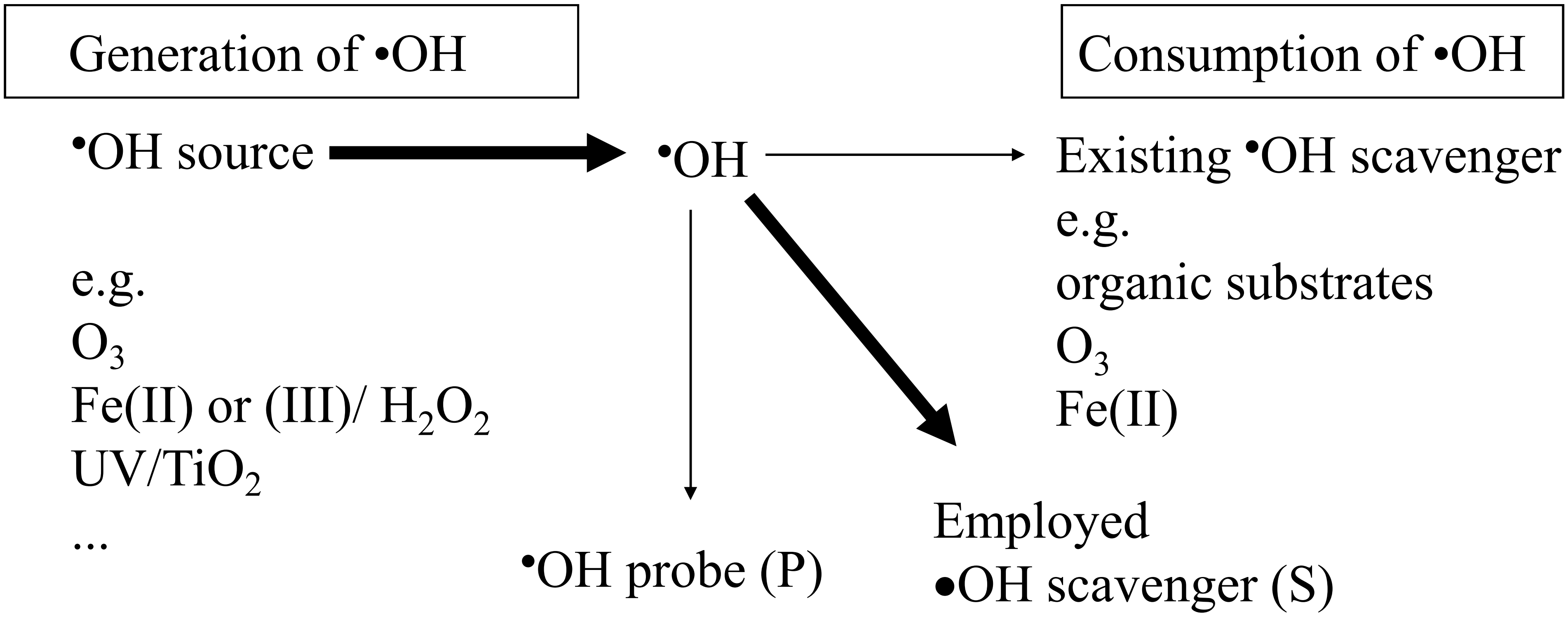
•OH source → •OH + excess P (probe compound) → A (product)

Let r_{OH}= the •OH generation rate,

$$d[{}^{\bullet}OH]/dt = r_{OH} - (-d[P]/dt) \approx 0$$

$$r_{OH} = -d[P]/dt = d[A]/dt$$

(2) Use of excess •OH scavenger & trace amounts of •OH probe compound



Generation of •OH

•OH source

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

•OH

Consumption of •OH

Existing •OH scavenger
e.g.
organic substrates
O_3
Fe(II)

•OH probe (P)

Employed
•OH scavenger (S)

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

Use of excess •OH scavenger & trace amounts of •OH probe compound

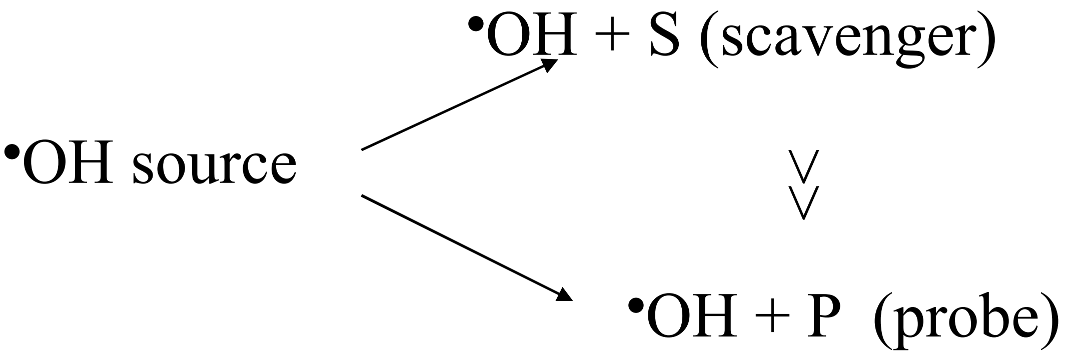
1. •OH 과 빠른 속도로 반응하고 그 속도상수를 알고 있는 화합물 중 •OH probe compound (k_p)와 •OH scavenger (k_s)를 하나씩 선정

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

2. 시스템 내 농도를 알고 있는 과량의 •OH scavenger 와 미량의 •OH probe compound를 가함.

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

3. 실험을 통해 측정한 •OH probe compound 의 일차분해 속도로부터 •OH 생성속도를 구한다.



•OH + S (scavenger)

•OH source

∨
∨

•OH + P (probe)

Let r_{OH}= the •OH generation rate,

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

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

Then, $d[P]/dt = k_{p,obs}[P] = k_p[{}^{\bullet}OH]_{ss}[P]$

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

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

Probe compound의 분해시간 동안 scavenger의 농도는 변하지 않는다고 가정

Measuring r_{OH}

예제 : UV/H_2O_2 공정에서 •OH의 생성속도를 측정하기 위해 공정 초기에 과량의 t-BuOH 10 mM (•OH scavenger)과 미량의 pCBA 2 μM (•OH probe compound)를 첨가하여 pCBA의 감소를 살펴보았다. •OH생성속도는 ?

(pCBA와 •OH의 반응 속도상수; 5×109 M-1 s-1
t-BuOH과 •OH의 반응 속도상수; 6.6×108 M-1 s-1).

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

Measurement of r_{OH}

Form the linear relationship between $\ln([pCBA]_0/[pCBA])$ and time, find out $k_{pCBA,obs.}$

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

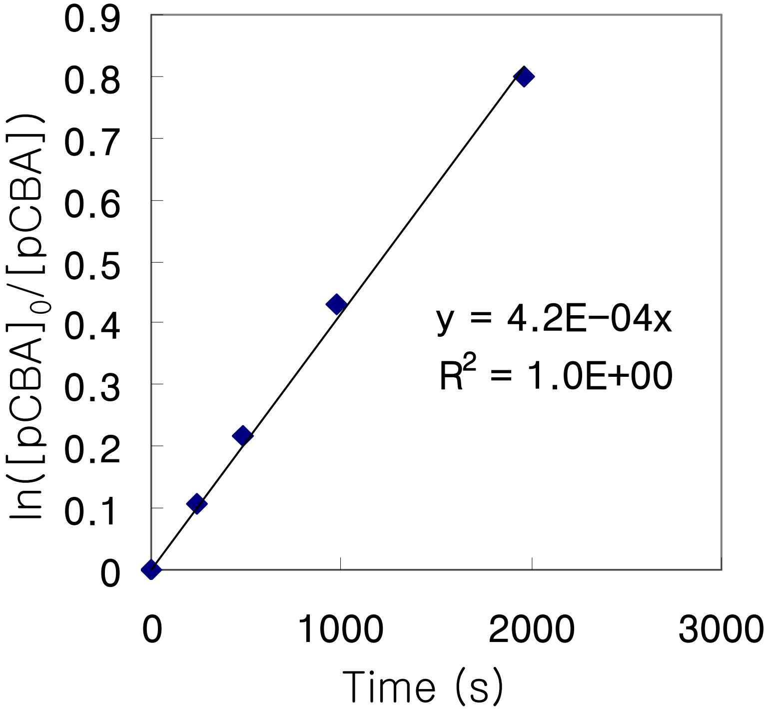
$$\Rightarrow d[pCBA]/[pCBA] = k_{pCBA,obs}\, dt$$

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

Measurement of r_{OH}

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

$\ln([pCBA]_0/[pCBA])$
0
0.11
0.22
0.43
0.80



From slope, $k_{pCBA,obs} = 4.2\times10^{-4}\ s^{-1}$

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

$$r_{OH} = (6.6\times10^{8}\ M^{-1}\ s^{-1}) \times (4.2\times10^{-4}\ s^{-1}) \times (10^{-2}\ M) / (5\times10^{9}\ M^{-1}\ s^{-1})$$
$$= 5.5\times10^{-7}\ M\ s\text{-}1$$