Ozonation of Water and Wastewater

- molecular mass: 48.0 g
- melting point: −193 °C
- UV absorption band in water:

  ε_{max} at 258 nm: 3150 M^{-1} cm^{-1} [15] (this broad absorption band extends up into the region of 300 nm)
- visible absorption band:

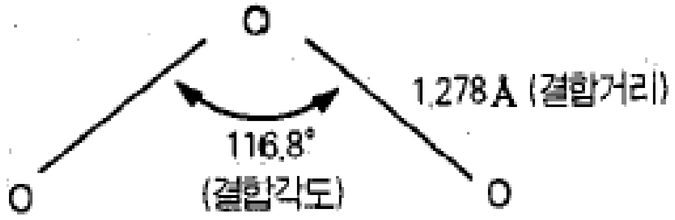
  ε_{max} at 600 nm: about 1.2 M^{-1} cm^{-1} (calc. from ε_{gas}); concentrated solutions of O_3 appear blue
- Henry constants:

  K_H (0 °C): 35 atm/(mol/l);
  K_H (20 °C): 100 atm/(mol/l);
- instant odor threshold conc. in air: about 40 µg m^{-3}, but adaptation takes place within minutes [16];
- Maximal allowable conc. of ozone in air:

  < 200 µg m^{-3} air (about 0.1 ppmv) for an 8-hour working day (comparable limits set by different countries); 240 µg m^{-3} in air are considered as nasal toxicant lowest observable level [17];
  about 100 µg m^{-3} air is the tropospheric threshold conc. for effects on plants (tobacco, etc.) [18]);
- Redoxpotential in aqueous solution:

  $(O_3)_{gas} + 2H^+ + 2e^- \rightarrow (O_2)_{gas} + H_2O \quad E_0^H = 2.07\ V$
  (for: pH = 0 and $[O_2/O_3]$ in gas), cf. [19].

Ozone



- The name of ozone is derived from the ‘ozein’, which is a Greek word and means to smell

- Strong oxidizing agent (2.07 V), eye and skin irritation in high concentration

- Structure of ozone (O_3) (resonance structure); eletrophilic & nucleophilic, MW: 48

- Unstable. Auto decomposition in water as well as in air. Half life : 20-30 min at 20℃

OH radical is generated in decomposition reaction, faster decomposition occurs in basic condition.

- maximum absorption wavelength: 250 nm (gas), 260 nm (water, ε = 3150 M-1.cm-1)

H (Henry contants): 100 atm/M (20℃), 35 atm/M (0℃)

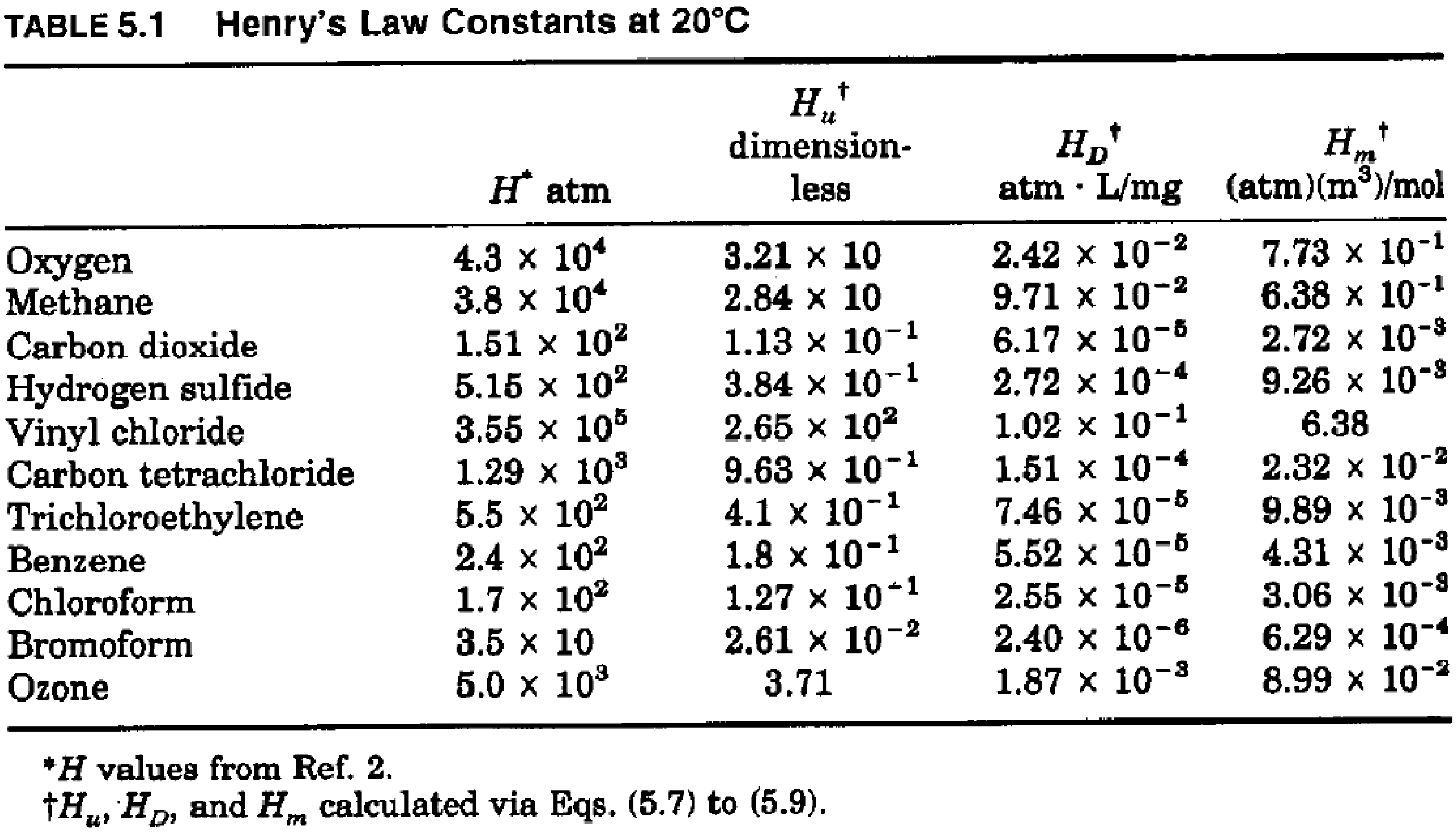


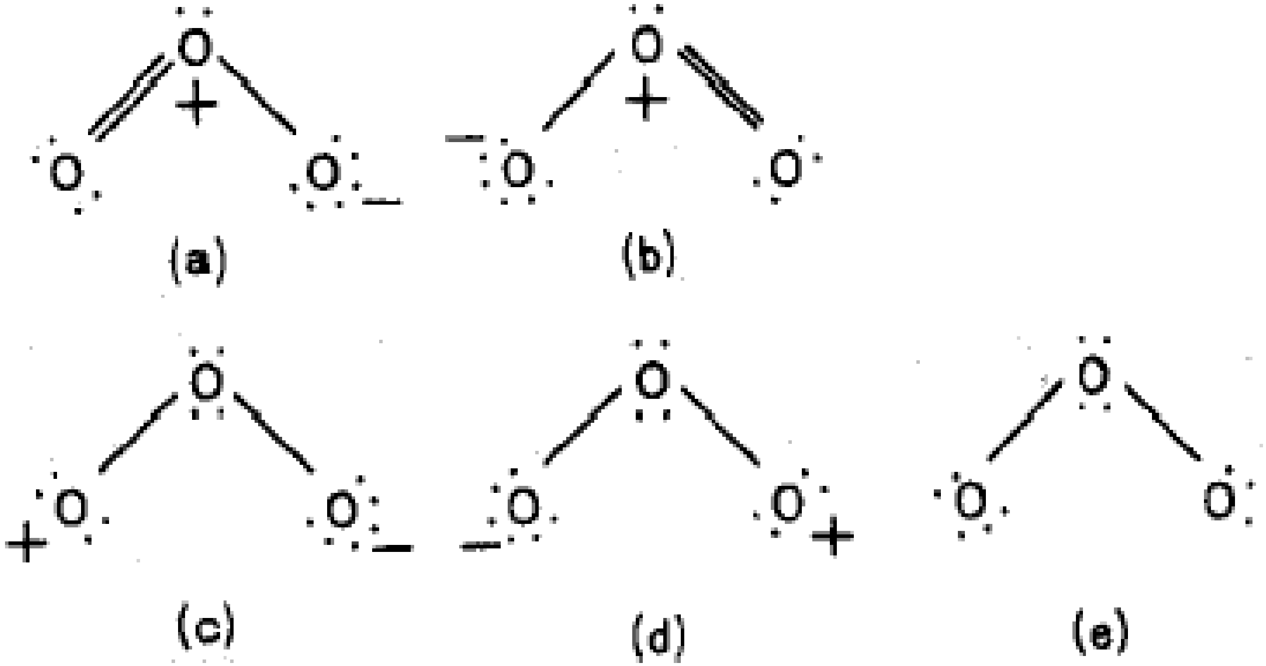
TABLE 5.1 Henry's Law Constants at 20°C

	H^* atm	$H_u^\dagger$ dimensionless	$H_D^\dagger$ atm · L/mg	$H_m^\dagger$ (atm)(m^3)/mol
Oxygen	4.3×10^4	3.21×10	2.42×10^{-2}	7.73×10^{-1}
Methane	3.8×10^4	2.84×10	9.71×10^{-2}	6.38×10^{-1}
Carbon dioxide	1.51×10^2	1.13×10^{-1}	6.17×10^{-5}	2.72×10^{-3}
Hydrogen sulfide	5.15×10^2	3.84×10^{-1}	2.72×10^{-4}	9.26×10^{-3}
Vinyl chloride	3.55×10^5	2.65×10^2	1.02×10^{-1}	6.38
Carbon tetrachloride	1.29×10^3	9.63×10^{-1}	1.51×10^{-4}	2.32×10^{-2}
Trichloroethylene	5.5×10^2	4.1×10^{-1}	7.46×10^{-5}	9.89×10^{-3}
Benzene	2.4×10^2	1.8×10^{-1}	5.52×10^{-5}	4.31×10^{-3}
Chloroform	1.7×10^2	1.27×10^{-1}	2.55×10^{-5}	3.06×10^{-3}
Bromoform	3.5×10	2.61×10^{-2}	2.40×10^{-6}	6.29×10^{-4}
Ozone	5.0×10^3	3.71	1.87×10^{-3}	8.99×10^{-2}

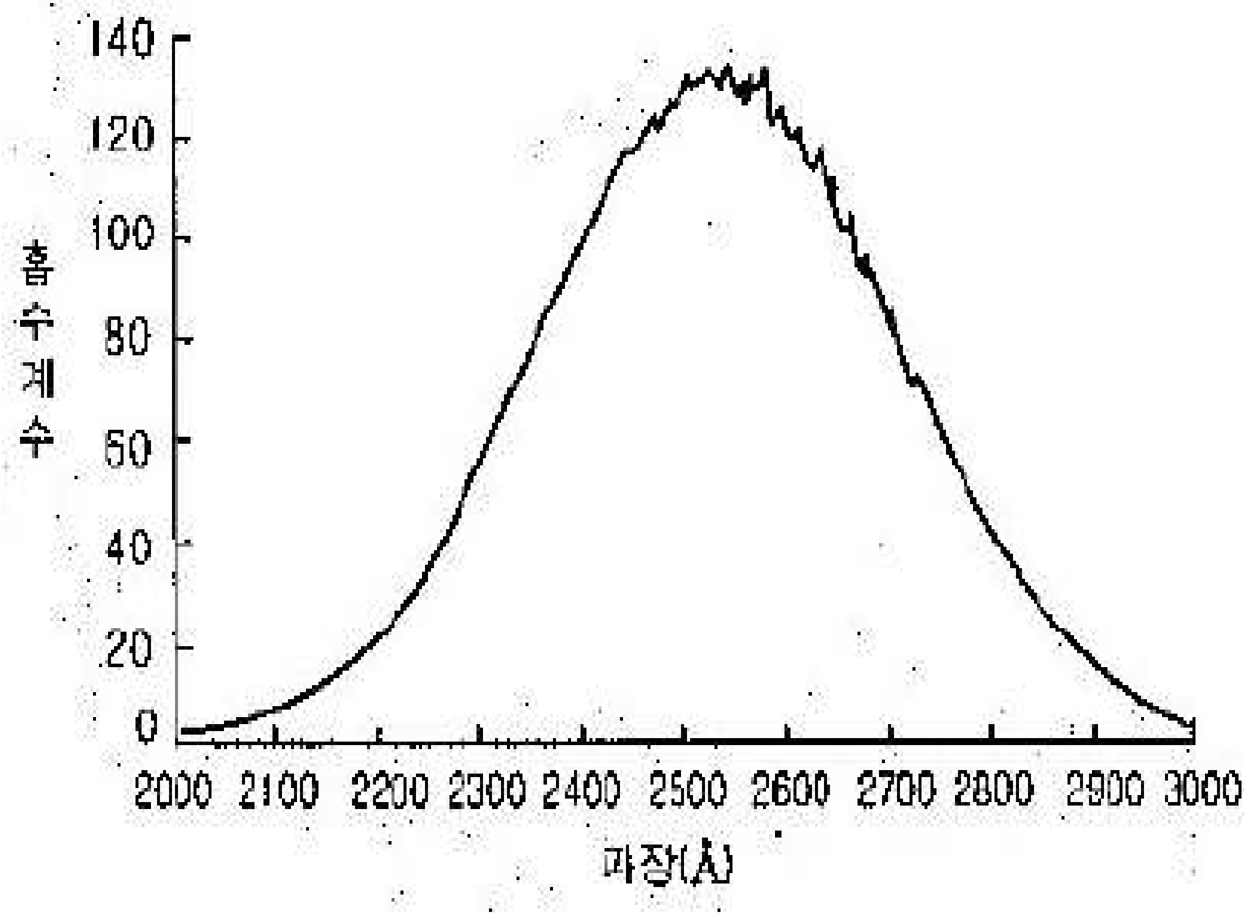
*H values from Ref. 2.

†H_u, H_D, and H_m calculated via Eqs. (5.7) to (5.9).

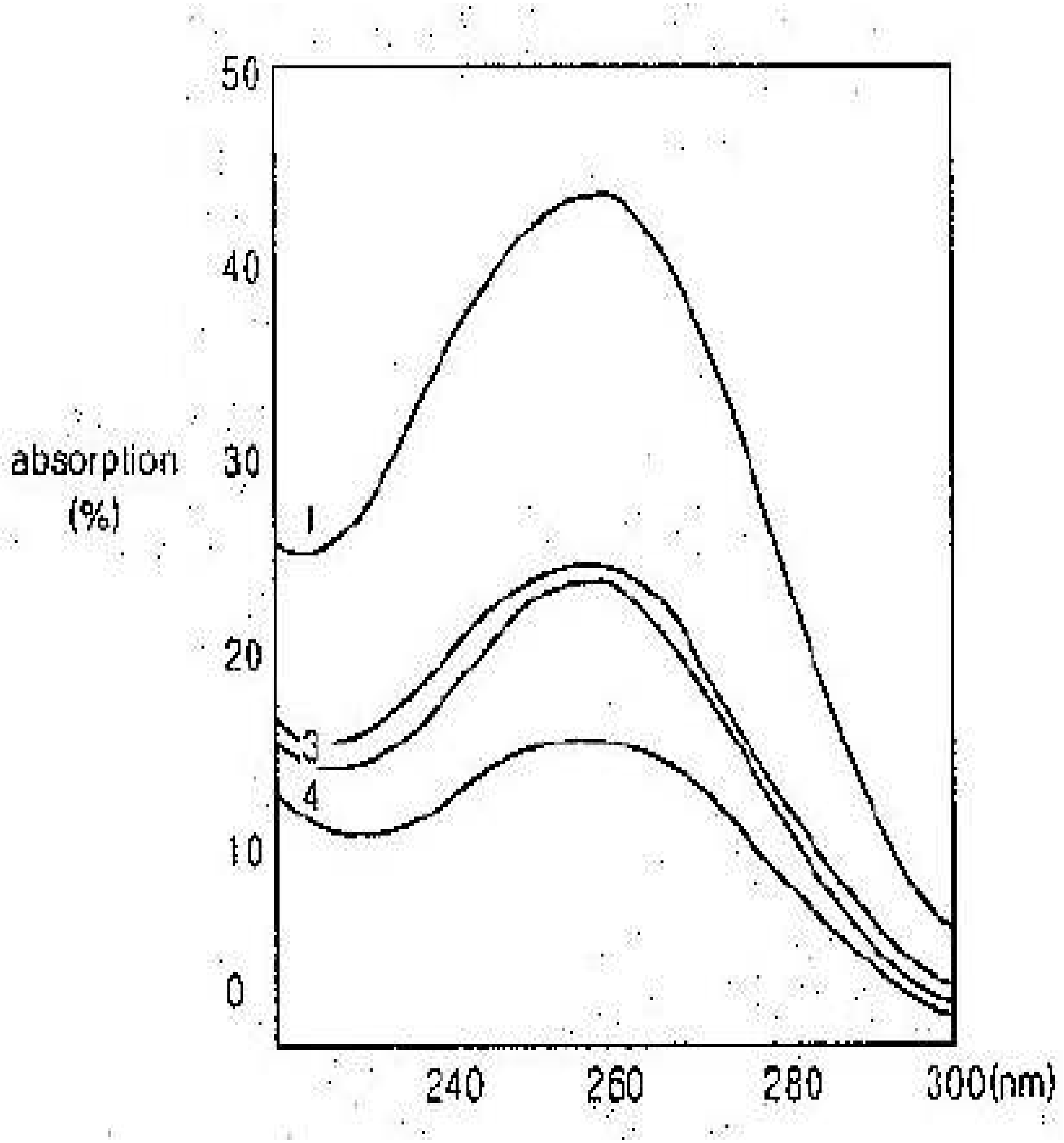
Resonance structure of ozone



Absorption spectrum of ozone Hartley band (gas phase)



Absorption spectrum of ozone (O_3) in water



1: 2.58×10^{-4} M (12.4 mg/L),

2: 1.29×10^{-4} M,

3: 1.20×10^{-4} M,

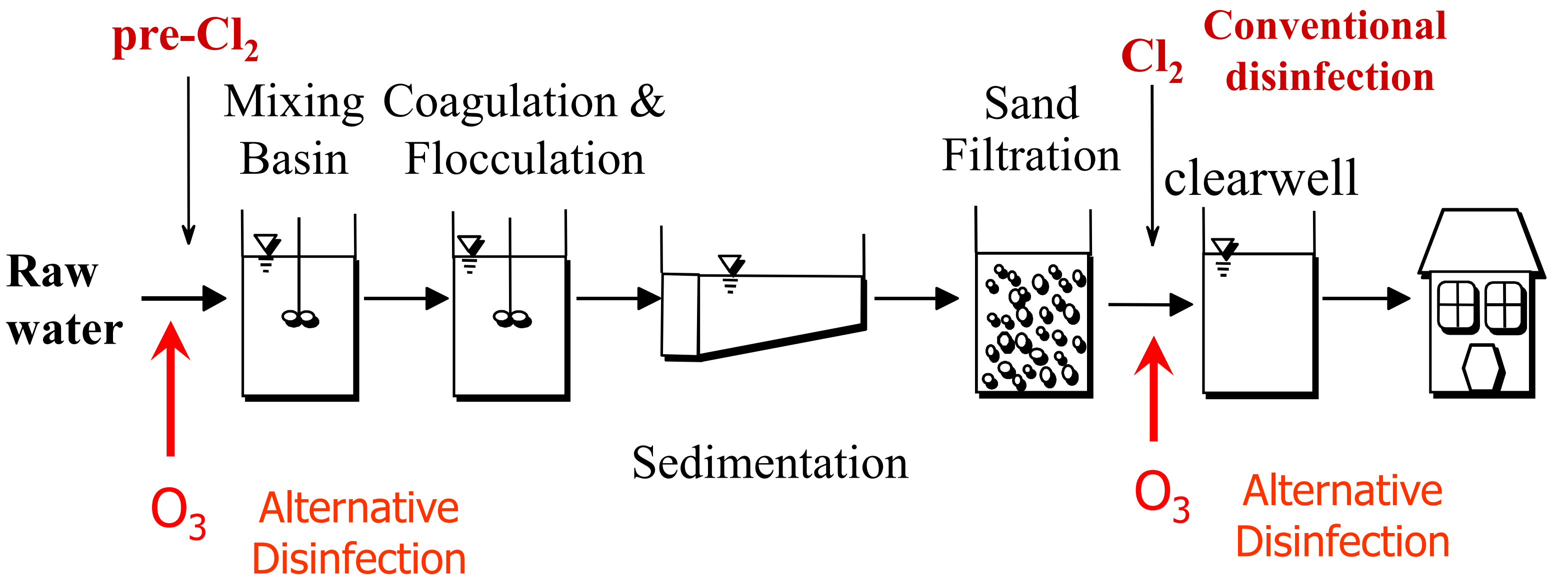
4: 0.775×10^{-4} M

Application of ozone in water and waste water

- Drinking water treatment
- Waste water
- Sewage water
- Water reclamation

Application of ozone in water treatment

- Water treatment process



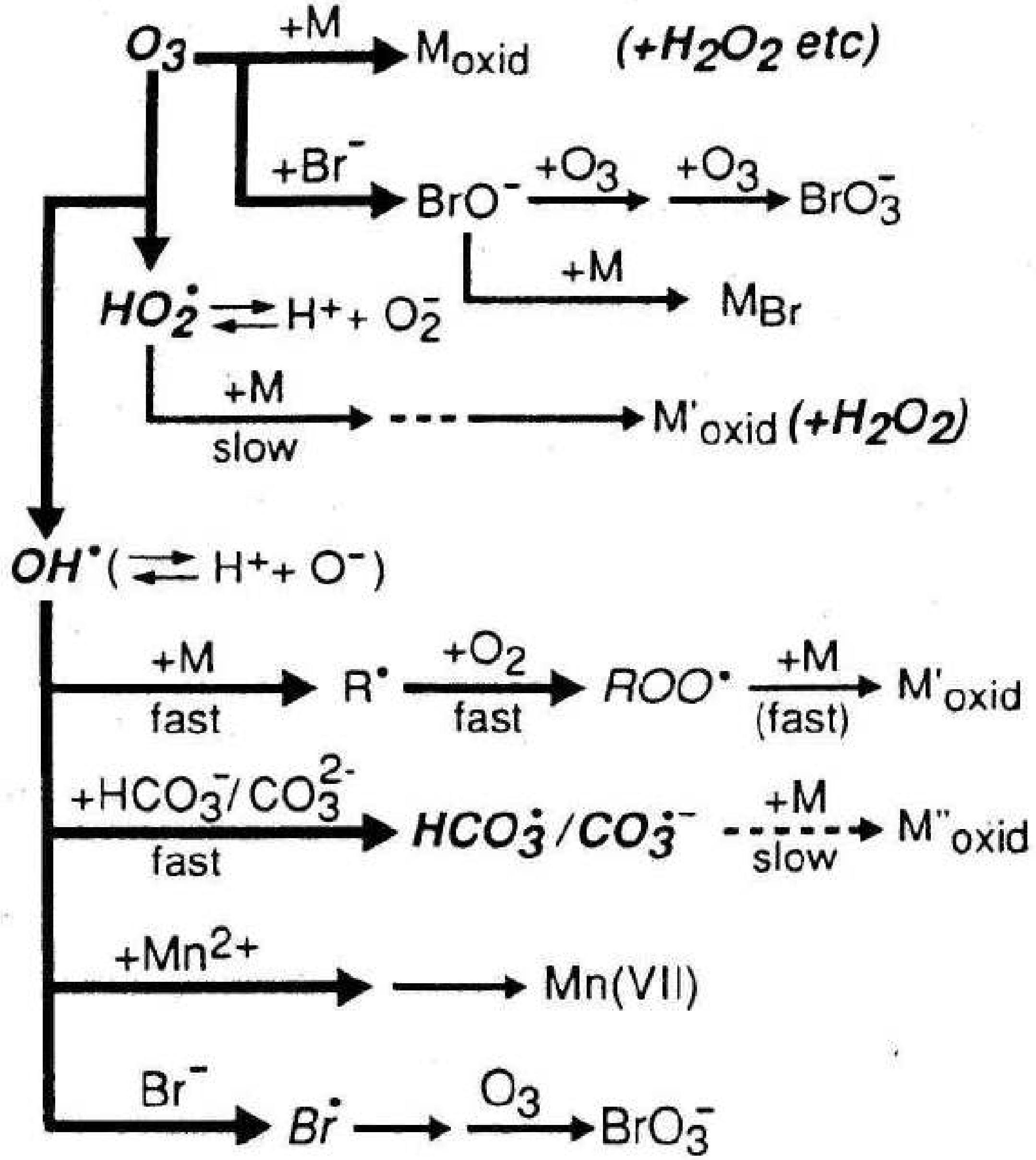
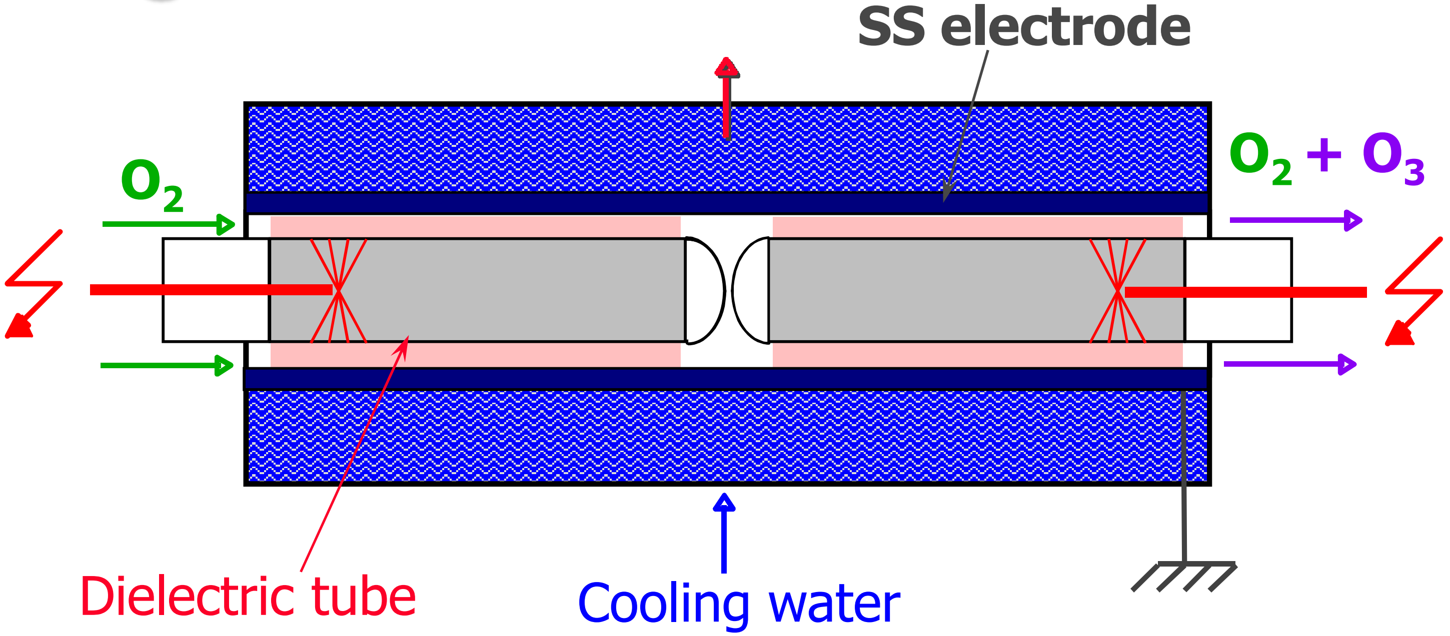


Fig. 2. Direct reactions of ozone with solutes (M or Br^-) and reactions of dominant secondary oxidants (adapted from [20])

Water treatment plants using ozonation process

수계	정수장명	취수원	시설용량 (톤/일)	고도정수공정	사업비 (백만원)	진행사항	비고
한강	동두천	한탄강표류수	60,000	입상활성탄	6,701	운전중	-
	원주 제2	섬강표류수	85,000	활성탄	11,750*	운전중	-
	인천 부평	한강 잠실	500,000 (130,000)	산소, 활성탄		운전중	2006년까지 오존 및 활성탄 시설추가 도입예정
낙동강	부산 화명	낙동강	600,000	전·후오존 활성탄		운전중	오존시설 노후화로 교체 및 보수 고려중
	부산 덕산	매리취수장	1,555,000 (1,050,000)	전·후오존 활성탄	114,500	운전중	-
	부산 명장	회동정수장	277,000	전·후오존 활성탄	22,166	운전중	-
	대구 두류 (낙동강제1수원지)	강정취수장	310,000	후오존, 활성탄	27,400	운전중	전오존시설은 도입계획중
	대구 매곡 (낙동강제2수원지)	매곡취수장 (다사취수장)	800,000	후오존, 활성탄	63,800	운전중	전오존시설은 도입계획중 활성탄 재생시설 포함
	경산 하양	강정취수장	10,000	활성탄	980	운전중	-
	마산 칠서	칠서취수장	400,000	전·후오존 활성탄	33,520	운전중	-
	진해 석동	성주취주장 본포수원지	70,000	전·후오존 활성탄	10,275*	운전중	-
	김해 삼계	창암취수장	105,000	전·후오존 활성탄	12,440	운전중	-
	양산 범어	물금취수장	37,500	후오존, 활성탄	7,068	운전중	-
	양산 웅상	원동취수장	55,000	후오존, 활성탄	11,400	운전중	-
	울산 회야	회야댐, 원동취수장	270,000	후오존, 활성탄	20,622*	운전중	-
	울산 천상	대암댐	60,000	후오존, 활성탄	34,380*	운전중	-
금강	공주 옥룡	금강표류수, 복류수	28,000	전·후오존 활성탄	8,904	운전중	-
	군산 제2	대아저수지	25,000	분말, 입상활성탄	5,678*	운전중	분말활성탄주입시설은 38,000톤/일 용량

Ozone generation



Ozone generation

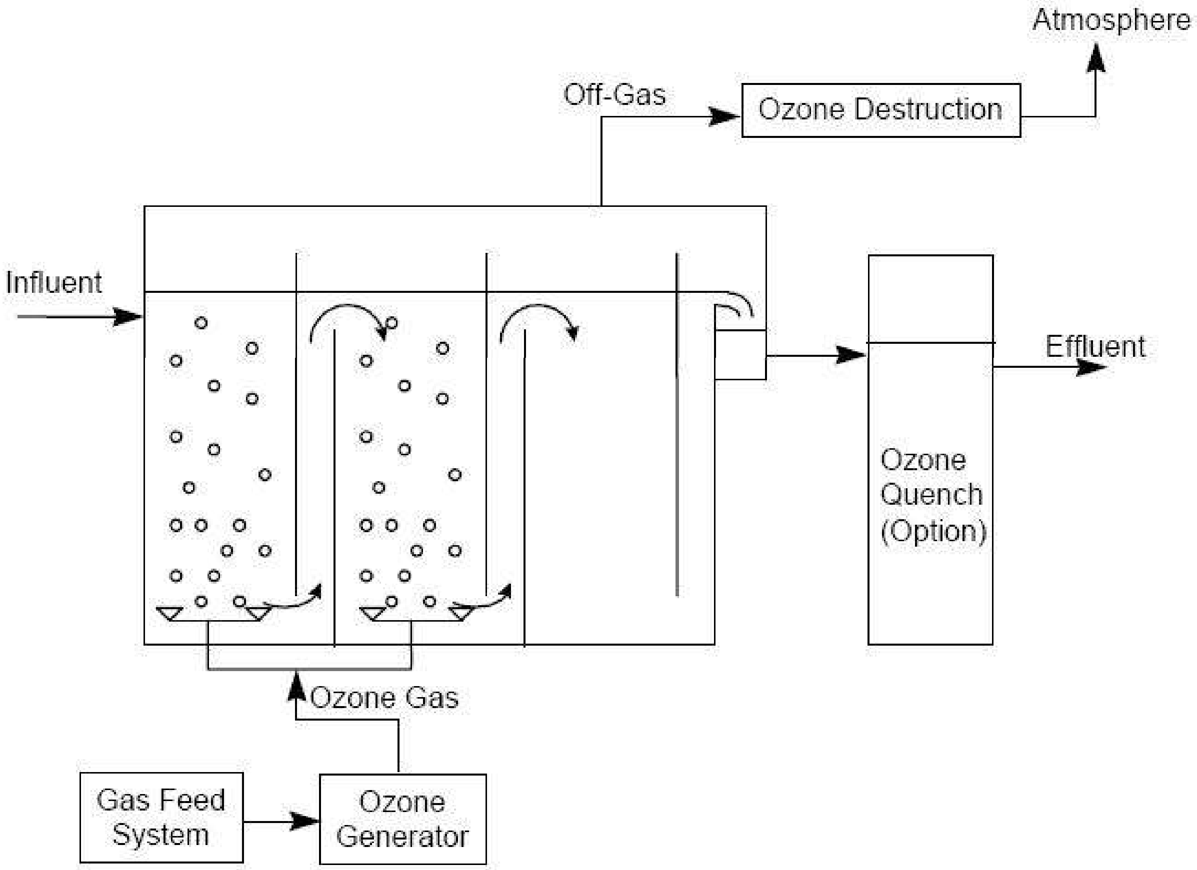
Firstly, ozone was synthetically discovered through the electrolysis of sulfuric acid. Ozone can be produced Several ways, although one method, Corona discharge, predominates in Ozone generation industry

Corona discharge

Corona discharge consists of passing an oxygen-containing gas through two electrodes separated by dielectric and a discharge gap. These electrons provide the energy to disassociate the oxygen molecules, leading to the formation of ozone

Ozone system schematic

- **Simplified Ozone System schematic**



Four basic components

Ozone water treatment systems have four basic components;

A. Gas feed system

B. Ozone generator

C. Ozone contactor

D. Off-gas destruction system

Ozone system schematic

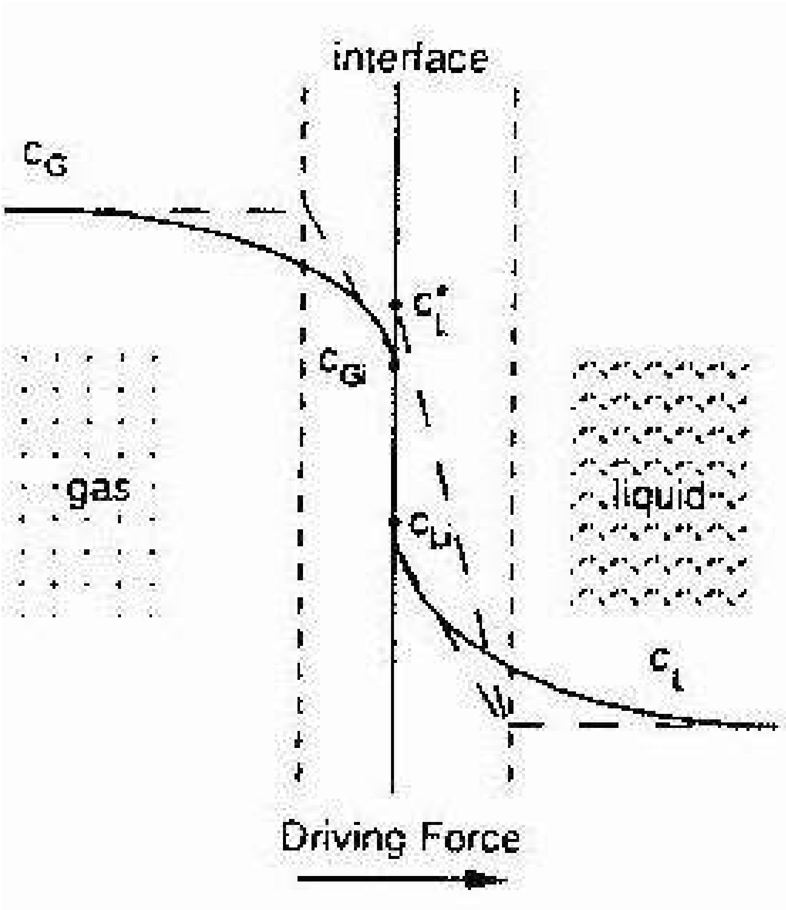
- **Duksan water treatment, Busan, Korea**

1. Ozone generator

2. Ozone contactor

Mass transfer in one phase

- **Two-film or two-resistance theory**



The resistance in each phase is made up of two parts: the diffusional resistance in the laminar film and the resistance in the bulk fluid.

$$k \propto D^n$$

k = film mass transfer coefficient
D = molecular diffusion coefficient
n = 0.1 ~ 1.0; depending on system turbulence

$$m = k_L a (c_{Li} - c_L)$$

m = specific mass transfer rate
$a = A/V_L$ = volumetric interfacial area
V_L = volume of liquid

2.1

Types of Molecular Ozone Reactions

2.1
Types of Molecular Ozone Reactions

b) *Oxygen-Atom Transfer Reactions*

$OH^- + O_3 \longrightarrow HO_2^- + O_2$ (3)

hydroperoxide anion

$Fe^{2+} + O_3 \longrightarrow FeO^{+2} + O_2$ (4)

$Fe^{(IV)}$

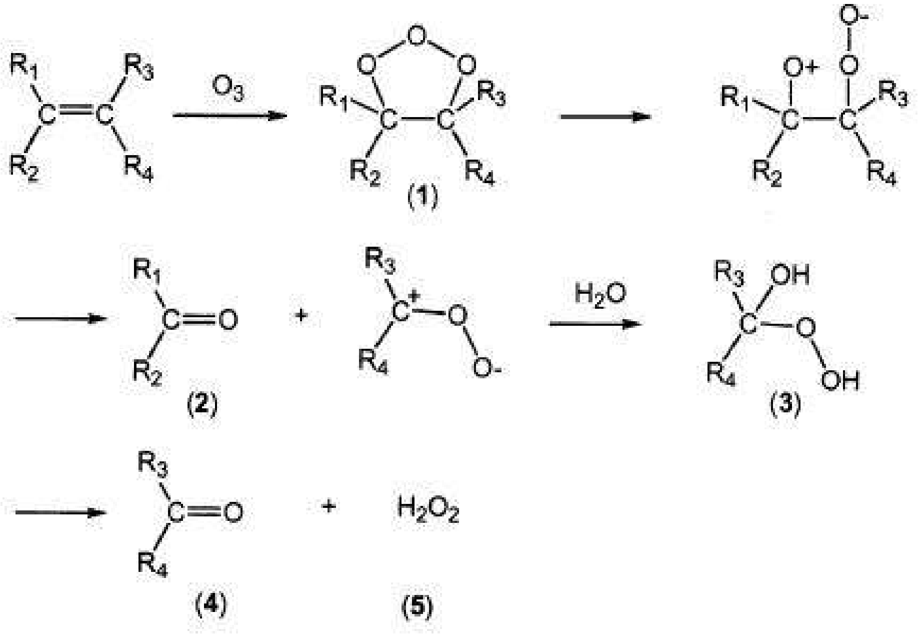
$NO_2^- + O_3 \longrightarrow NO_3^- + O_2$ (5)

2.1

Types of Molecular Ozone Reactions

Ozone oxidation

- **Reaction of olefines with ozone**

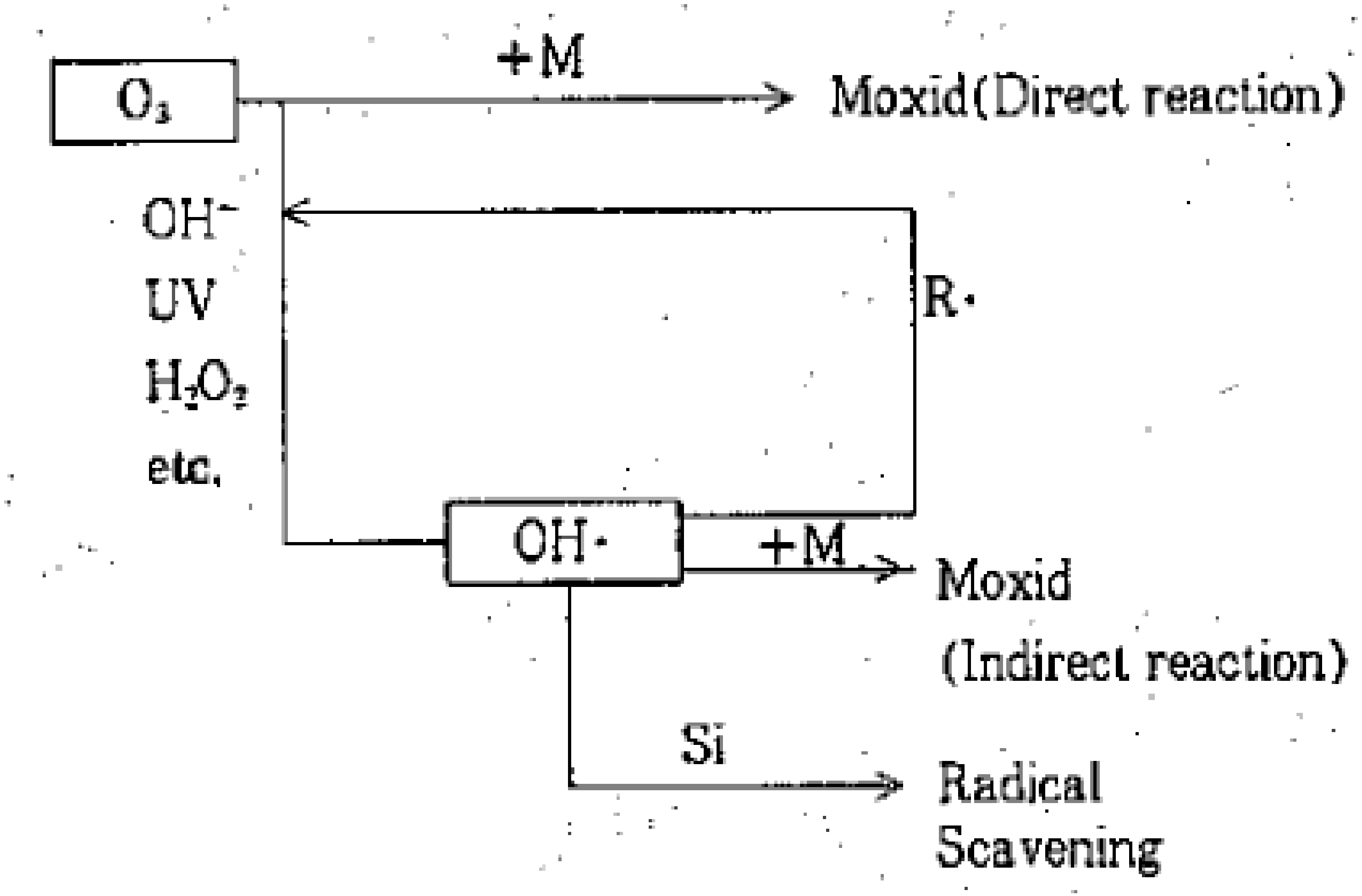


Initiation by the formation of an ozonide (1), an unstable cyclic trioxide

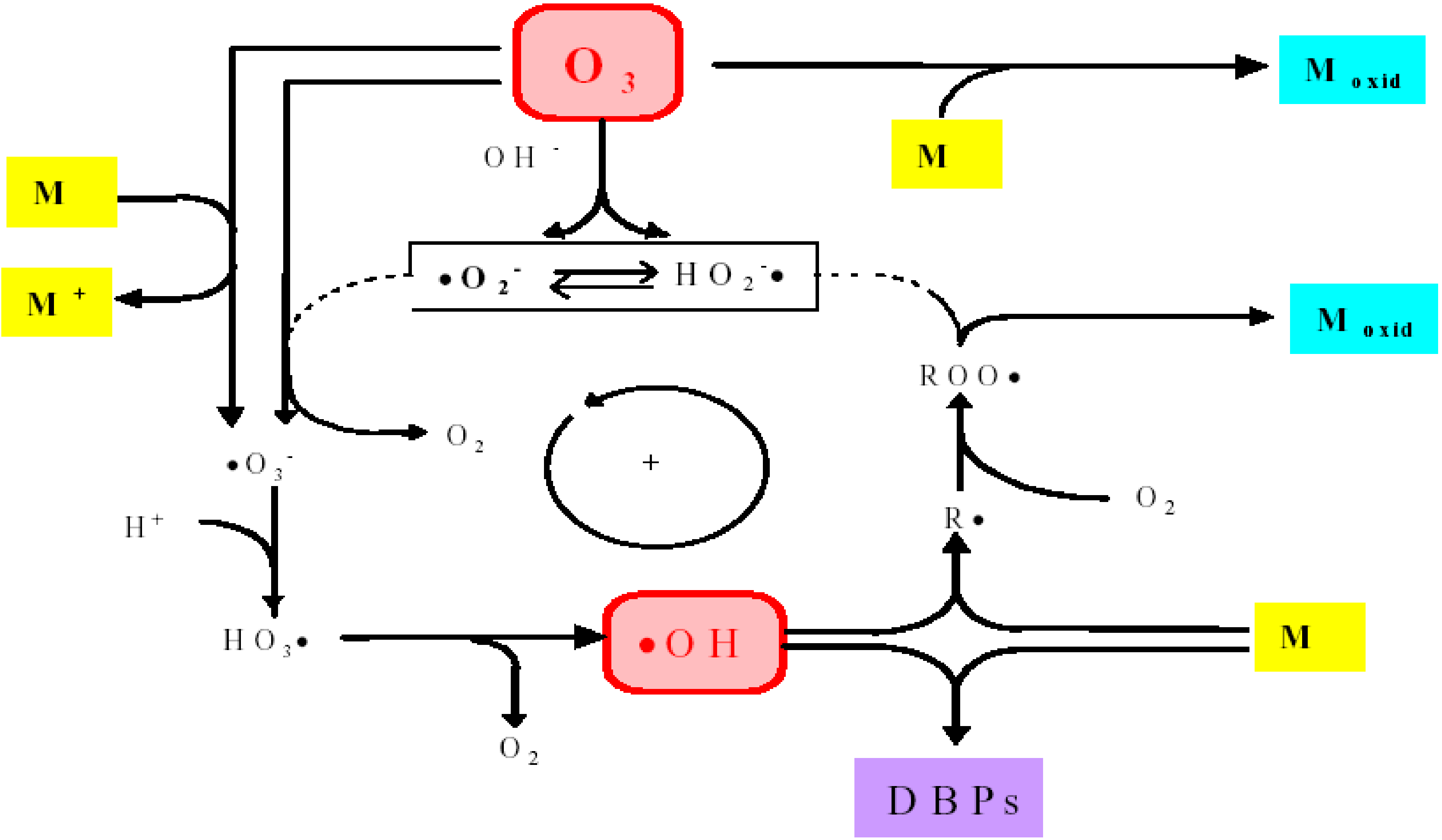
It decomposes into a carbonyl compound (2) and a hydroxyhydroperoxide (3)

This hydroxyhydroperoxide then slowly decomposes into a carbonyl compound (4) and hydrogen peroxide (5)

Organic removal pathway by ozone



Mechanism of Ozone Decomposition



$$\cdot OH + M \xrightarrow{k_{OH.M}} \qquad k_{OH.M} : 10^8 - 10^{10}\ M^{-1}s^{-1}$$

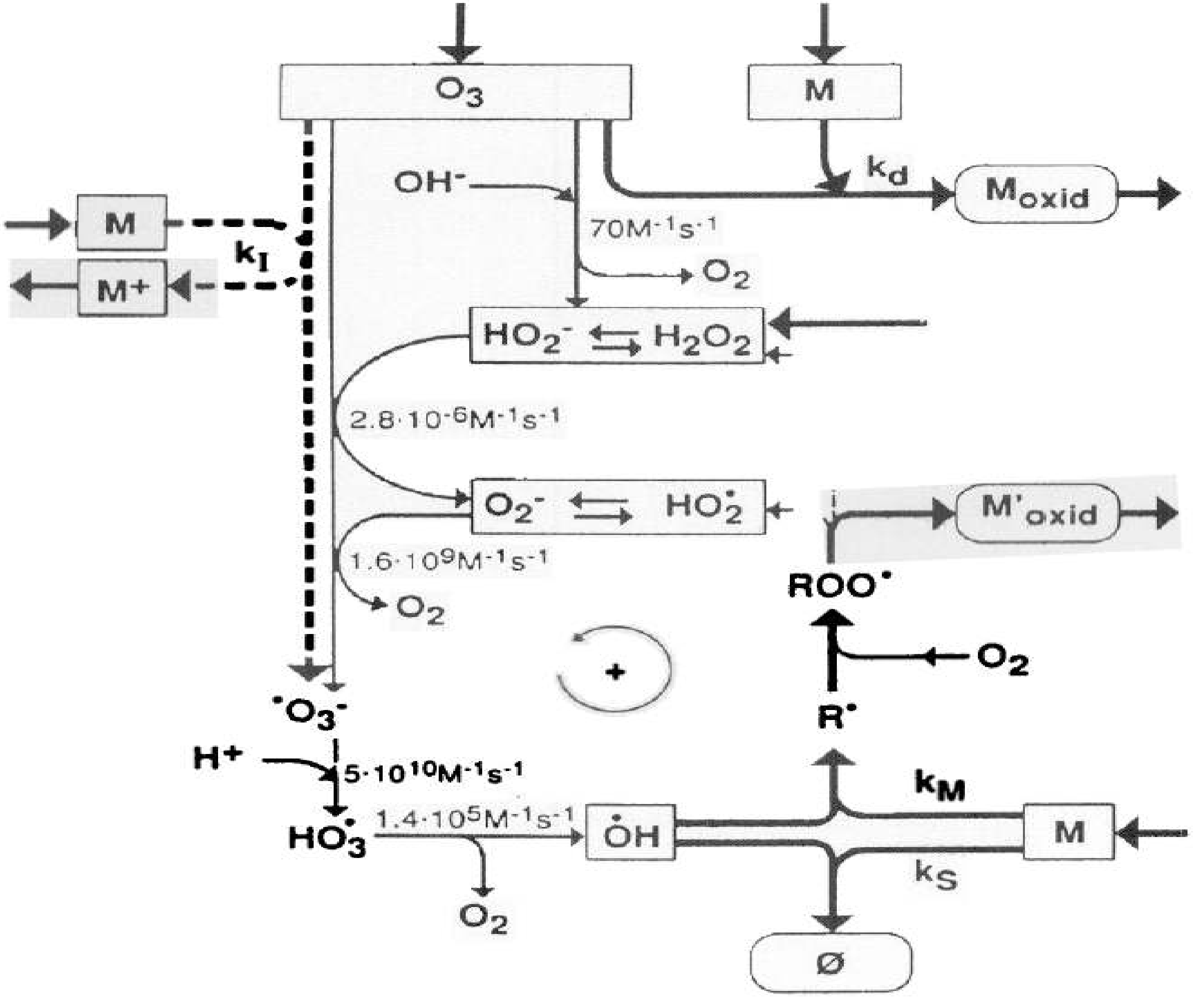
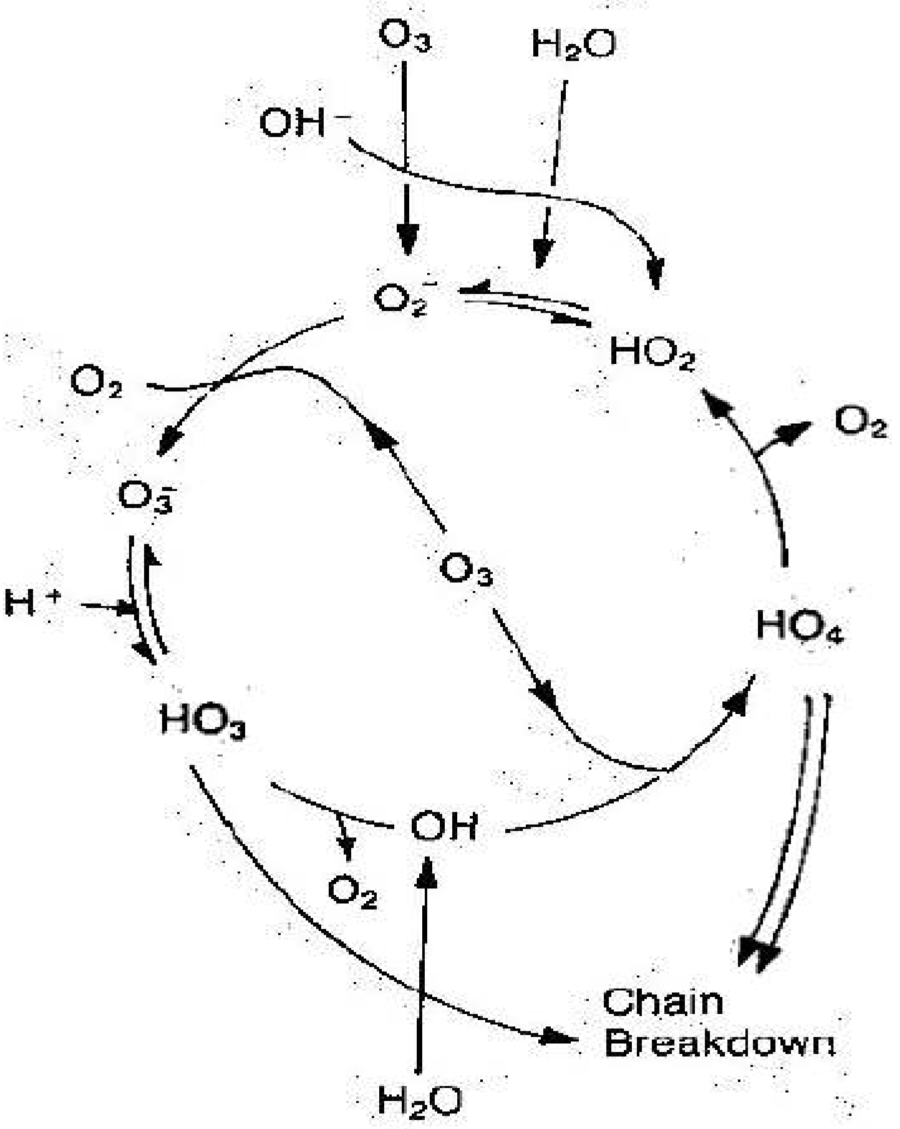


Fig. 8. Scheme of reaction of aqueous O_3. O_3 reacts either directly with a solute M (reaction-rate constant k_d) or it reacts with OH^- or M to initiate a radical-type chain reaction. Some types of M can also act as chain promoters by transforming non-selective $OH^\bullet$ into highly O_3 selective radicals (k_M), but some (e.g. bicarboante) can quench the chain reaction by just scavenging the chain carrier, $OH^\bullet$ (k_S). For further details see text. From [49], including newer data from [23]

Reaction Diagram and Rate Constants for Ozone Decomposition Process



Mechanism of ozone decomposition (Hoigne ´ mechanism)

The pH of the water is important because OH^- initiates ozone decomposition

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \qquad k = 70\ M^{-1}\ s^{-1}$$

$$O_3 + HO_2^- \rightarrow \cdot OH + O_2^{-\cdot} + O_2, \qquad k = 2.8 \times 10^6\ M^{-1}\ s^{-1}$$

$$O_3 + O_2^{-\cdot} \rightarrow O_3^{-\cdot} + O_2, \qquad k = 1.6 \times 10^9\ M^{-1}\ s^{-1}$$

The initiation of ozone decomposition can be artificially accelerated by increasing the pH or by the addition of hydrogen peroxide, which leads to an AOP (advanced oxidation processes)

pKa (H_2O_2) = 11.6

pKa ($HO_2\cdot$) = 4.8 Hydorperoxide radical, $O_2\cdot-$ **:** superoxide radical,

$O_3-\cdot$: ozonide radical (pKa = 6.1)

Mechanism of ozone decomposition

pH < 8 $O_3^{-\cdot} + H^+ \Leftrightarrow HO_3\cdot$, $k_+ = 1.6 \times 10^9\ M^{-1}\ s^{-1}$, $k_- = 3.3 \times 10^2\ s^{-1}$

$HO_3\cdot \rightarrow \cdot OH + O_2$, $k = 1.4 \times 10^5\ s^{-1}$

pH > 8 $O_3^{-\cdot} \Leftrightarrow O^{-\cdot} + O_2$, $k_+ = 2.1 \times 10^3\ M^{-1}\ s^{-1}$, $k_- = 3.3 \times 10^9\ s^{-1}$

$O^{-\cdot} \rightarrow \cdot OH + OH^-$, $k = 10^8\ s^{-1}$

$\cdot OH + O_3 \rightarrow HO_2\cdot + O_2$ $k = 0.1 \sim 2 \times 10^9\ M^{-1}\ s^{-1}$

The last reaction is a fast process and is important for waters with low scavenger concentration. It leads to the consumption of ozone and OH radicals and lowers the oxidation capacity in the system

Effect of bicarbonate on the stability of ozone

$\cdot OH + CO_3^{2-} \rightarrow CO_3^{\cdot -} + OH^-$ $k=3.9 \times 10^8\ M^{-1}S^{-1}$

$\cdot OH + HCO_3^- \rightarrow CO_3^{\cdot -} + H_2O$ $k=8.5 \times 10^6\ M^{-1}S^{-1}$

~ The presence of bicarbonates in the water may inhibit the free radical reaction chain, hence slowing down decomposition of ozone in the water

~

Mechanism of ozone decomposition

NOM (natural organic matter) can affect the ozone stability
It can either (i) directly react with ozone or indirectly affect its stability through scavenging.

$$(1)\ \mathbf{O_3 + NOM_1 \rightarrow NOM_{1ox}}$$

$$(2)\ \mathbf{O_3 + NOM_2 \rightarrow NOM_2^{+\cdot} + O_3^{-\cdot}}$$

These reactions are generally attributed to double bonds, activated aromatic systems, amines and sulfides

(3) $\cdot OH + NOM_3 \rightarrow NOM_3^{\cdot} + H_2O$ or $NOM_3^{\cdot} + OH^-$

$NOM_3^{\cdot} + O_2 \rightarrow NOM - O_2^{\cdot} \rightarrow NOM_3^{+} + O_2^{\cdot -}$

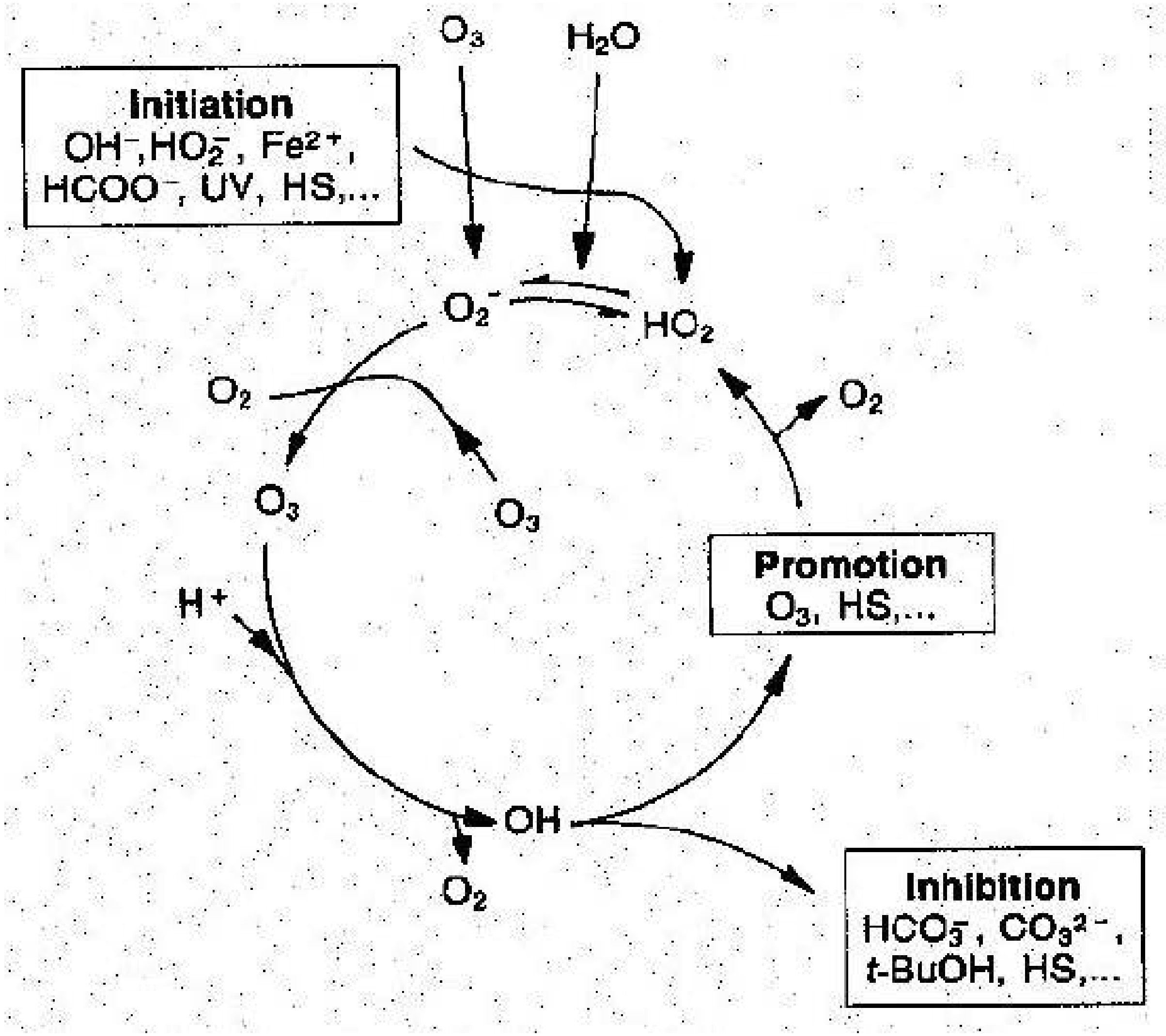
~ propagation reaction ➔ accelerated ozone decrease

(4) $\cdot OH + NOM_4 \rightarrow NOM_4^{\cdot} + H_2O$

$NOM_4^{\cdot} + O_2 \rightarrow NOM_4\text{-}O_2^{\cdot} \rightarrow$ no $O_2^{\cdot -}$ formation

~ Inhibitors are entities that do not liberate superoxide after reaction with OH radicals

Mechanism of Ozone Decomposition



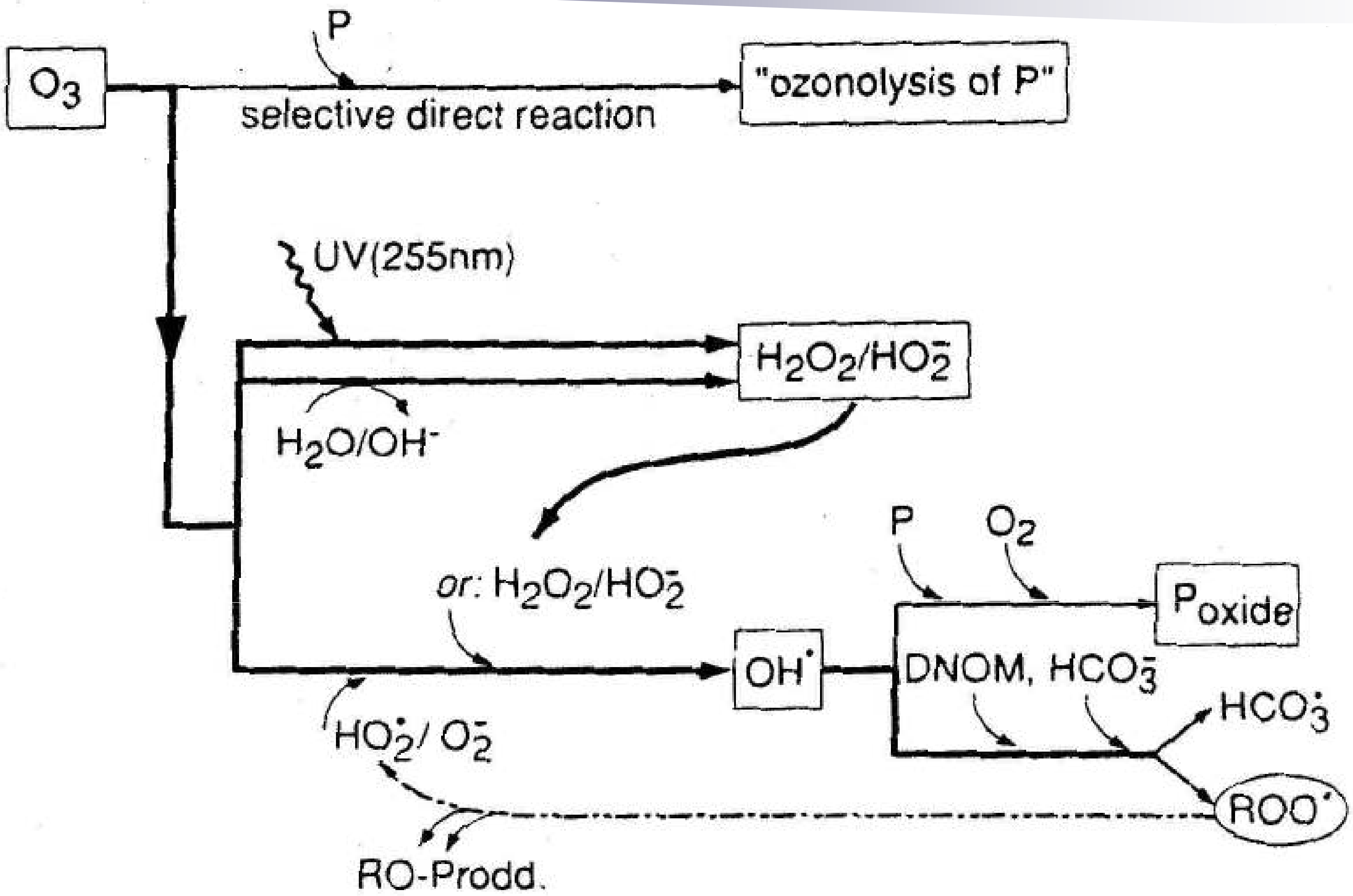


Fig. 9. Pathways for transformation of O_3 by reactions with pollutants (P), OH^-, H_2O_2, or by UV photolysis. Reactions with OH^- as well as UV photolyses produce primarily H_2O_2. In natural waters the initiated chain reaction is promoted by some reactions with DNOM and inhibited, e.g. by some other reactions with DNOM and by HCO_3^- (adapted and updated from [22]). Not shown is the initiation by activated carbon (cf. Sect. 7.5)

Ozone/Hydrogen Peroxide(O_3/H_2O_2)

$$H_2O_2 \leftrightarrow HO_2^- + H^+ \qquad pK_a = 11.8$$

$$HO_2^- + O_3 \rightarrow HO_2^\circ + O_3^{\circ-} \qquad k_9 = 2.2\ 10^6\ M^{-1}\ s^{-1}$$

$$H_2O_2 + O_3 \rightarrow H_2O + 2\ O_2 \qquad k_{10} < 10^{-2}\ M^{-1}\ s^{-1}$$

$$2\ O_3 + H_2O_2 \rightarrow 2\ OH^\circ + 3\ O_2$$

Ozone / H_2O_2

Hydrogen peroxide initiates the ozone decomposition by formation of OH radical and superoxide which further reacts with molecular ozone

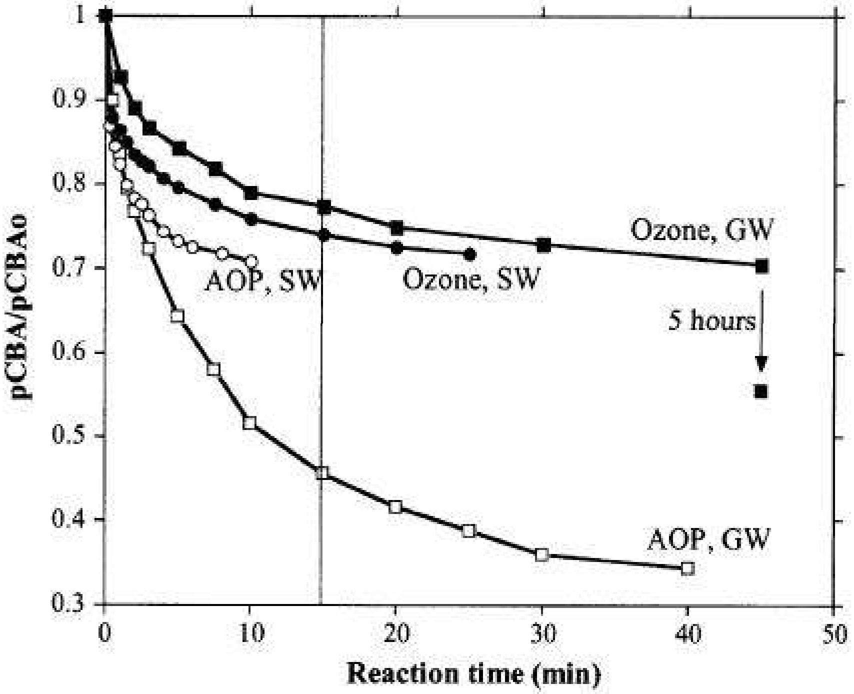
$$H_2O_2 + H_2O \Leftrightarrow HO_2^- + H_3O^+$$

$$HO_2^- + O_3 \rightarrow \cdot OH + O_2^{-\cdot} + O_2$$

The yield of this reaction sequence is one OH radical per decomposed ozone molecule. This is somewhat higher than the yield achieved in low DOC waters in conventional ozonation porcesses

Ozone / H_2O_2

- **Oxidation of pCBA with ozone and OH radical**



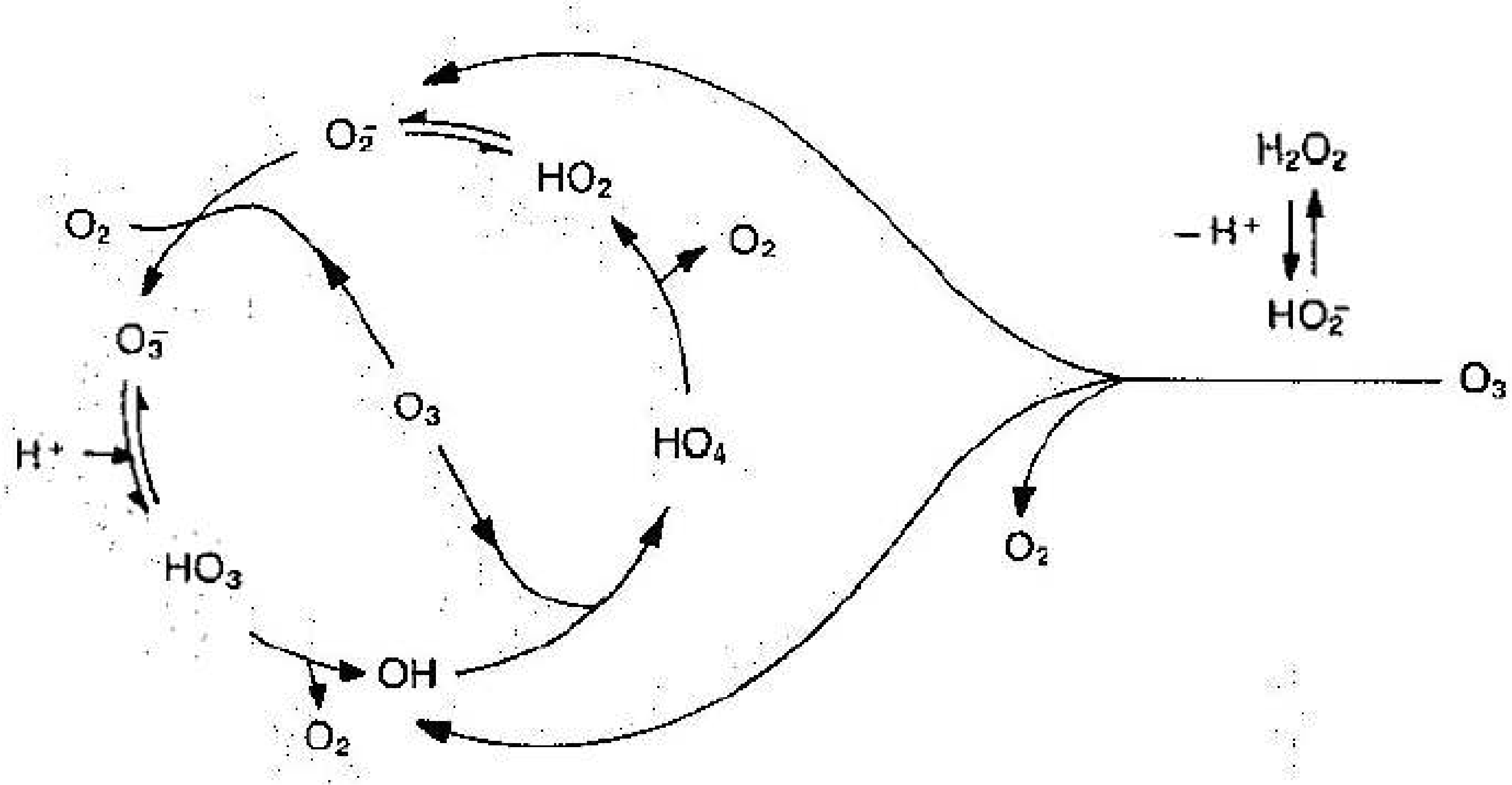
AOP : Ozone + H_2O_2

SW : Surface water

GW : Groundwater

The oxidation of pCBA is faster for both waters for the AOP. The degree of oxidation in the two waters is related to the concentration of scavengers in the water, i.e. higher in the surface water.

Ozone Decomposition Process by Hydroperoxide Ion



Ozone/ UV

$$O_3 + H_2O \xrightarrow{h\nu} H_2O_2 + O_2$$

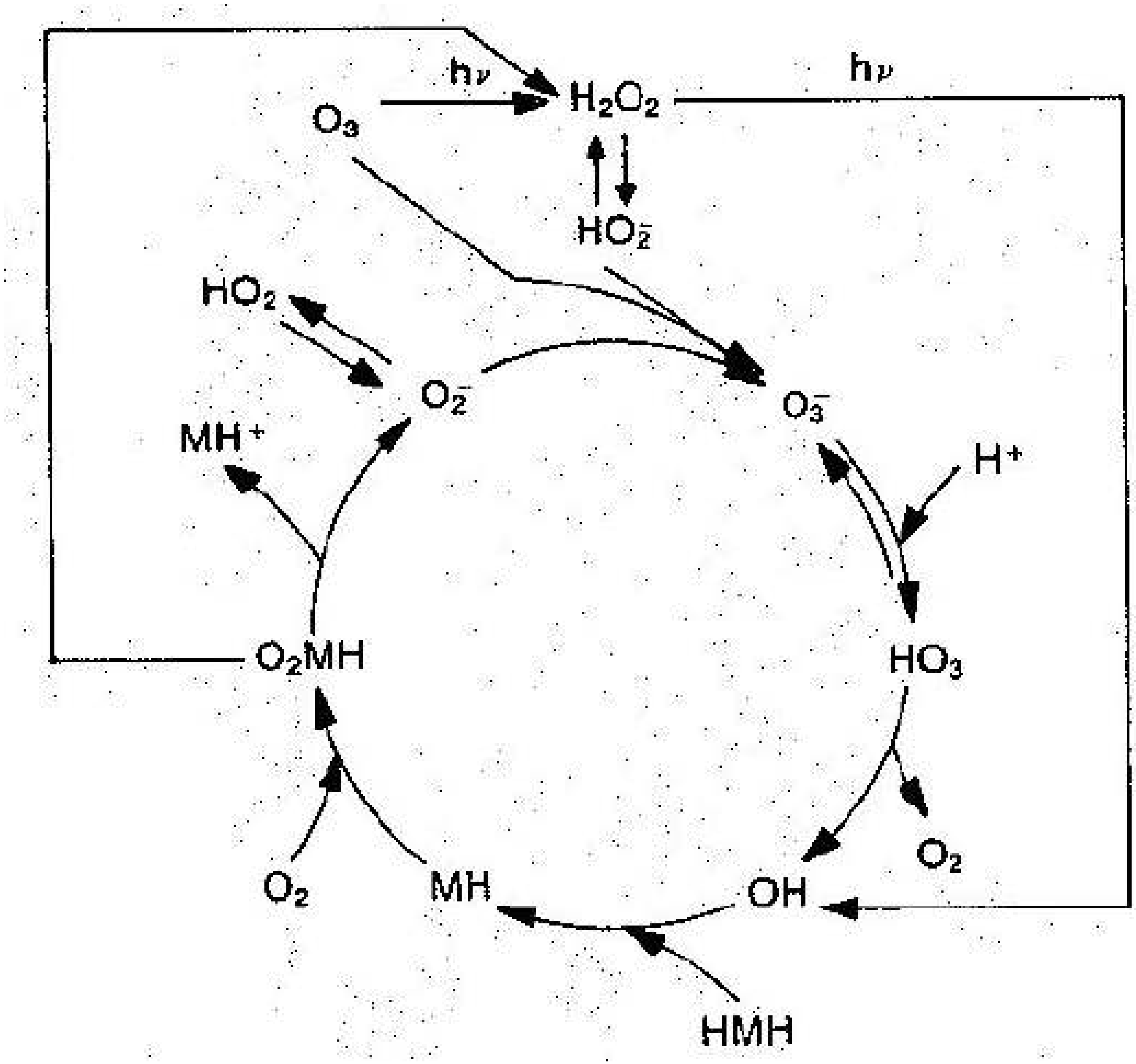
H_2O_2/UV

$H_2O_2 \xrightarrow{h\nu} 2\ OH^\circ$ $\qquad \varepsilon_{254\ nm} = 18.6\ M^{-1}\ cm^{-1}$

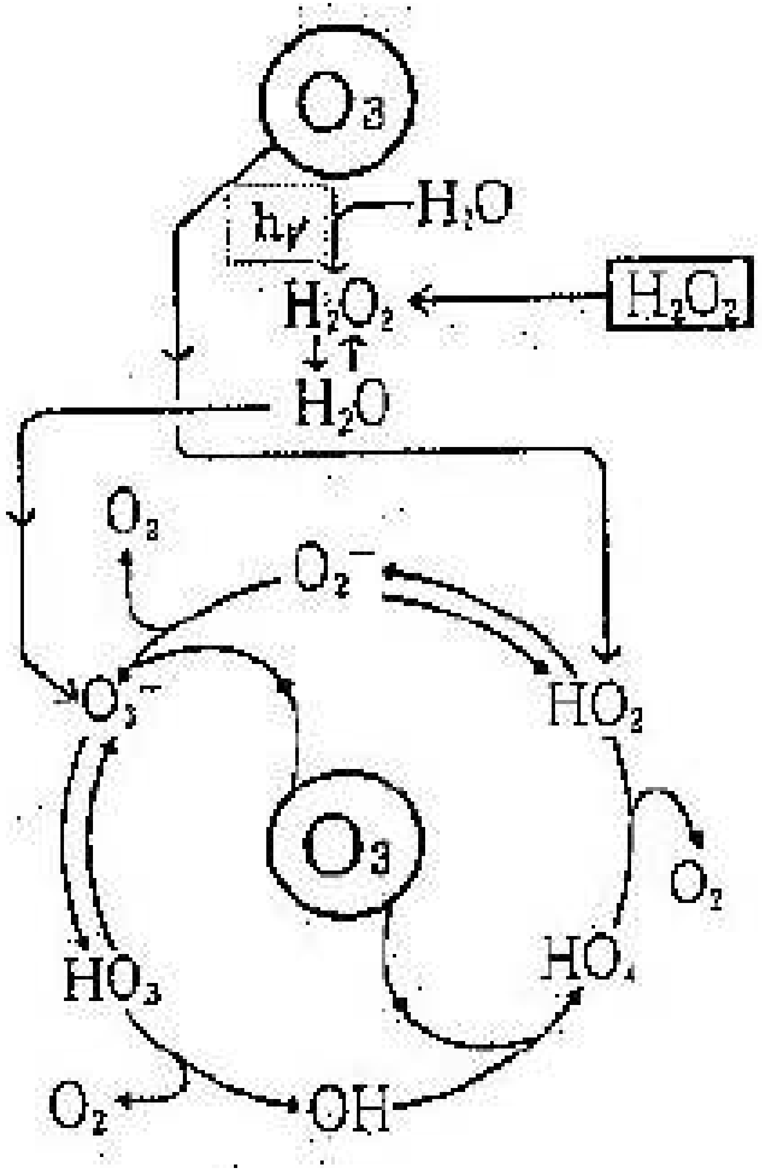
$HO_2^- \xrightarrow{h\nu} OH^\circ + O^{\circ-}$ $\qquad \varepsilon_{254\ nm} = 240\ M^{-1}\ cm^{-1}$

$HO_2^- + O^{\circ-} \rightarrow O_2^{\circ-} + OH^-$ $\qquad k_9 = 4.0\ 10^8\ M^{-1}\ s^{-1}$

Ozone Decomposition Process by Photolysis at 253.7 nm



Ozone/UV AOP & Peroxone AOP



Comparison of various AOPs

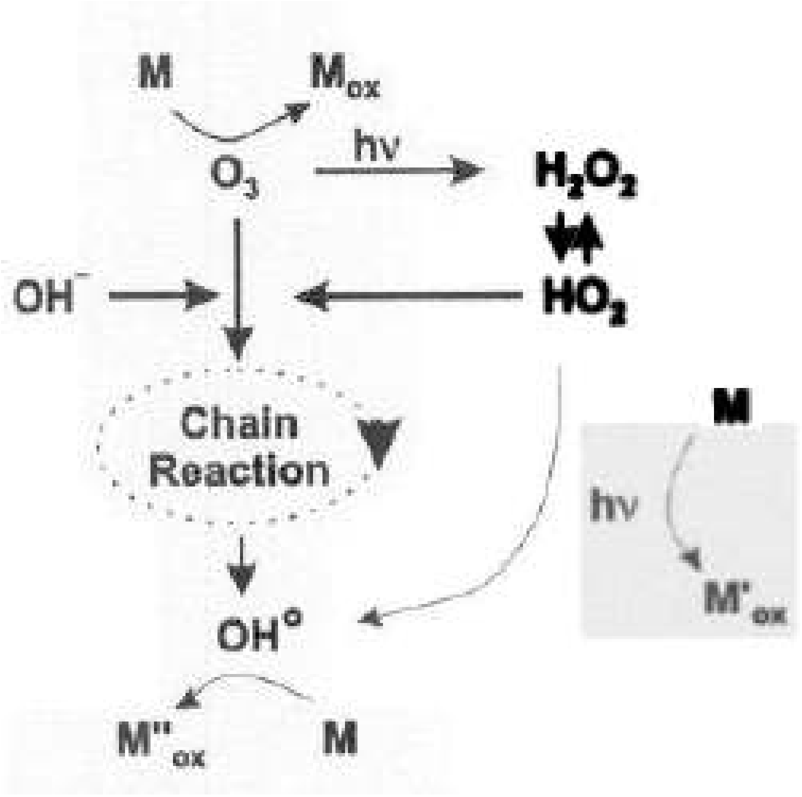


Figure 2-3: Advanced oxidation processes.

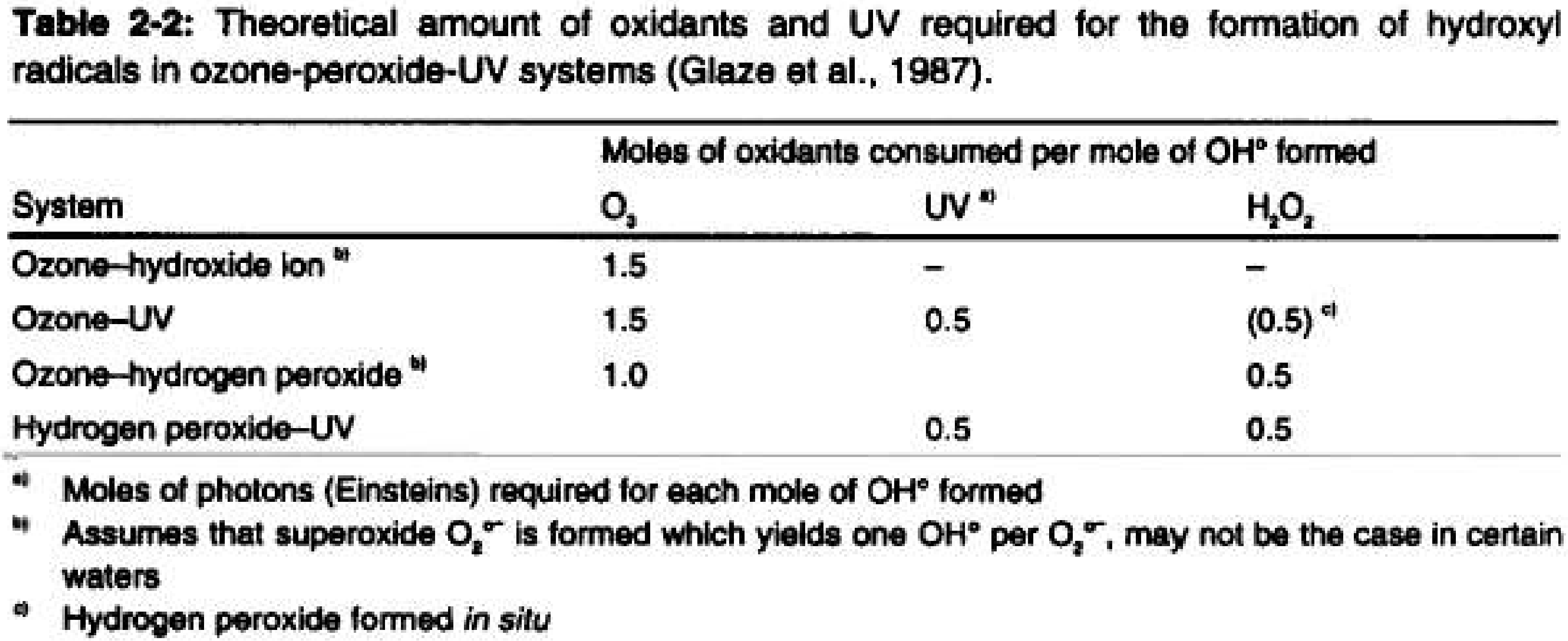


Table 2-2: Theoretical amount of oxidants and UV required for the formation of hydroxyl radicals in ozone-peroxide-UV systems (Glaze et al., 1987).

	Moles of oxidants consumed per mole of OH° formed		
System	O_3	UV [a]	H_2O_2
Ozone–hydroxide ion [b]	1.5	–	–
Ozone–UV	1.5	0.5	(0.5) [c]
Ozone–hydrogen peroxide [b]	1.0		0.5
Hydrogen peroxide–UV		0.5	0.5

[a] Moles of photons (Einsteins) required for each mole of OH° formed

[b] Assumes that superoxide $O_2^{\circ -}$ is formed which yields one OH° per $O_2^{\circ -}$, may not be the case in certain waters

[c] Hydrogen peroxide formed *in situ*

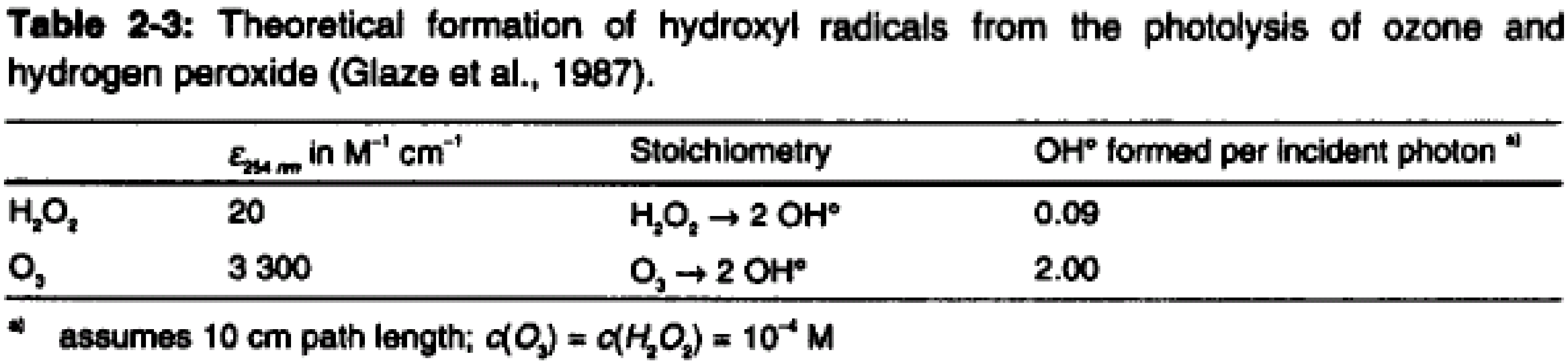
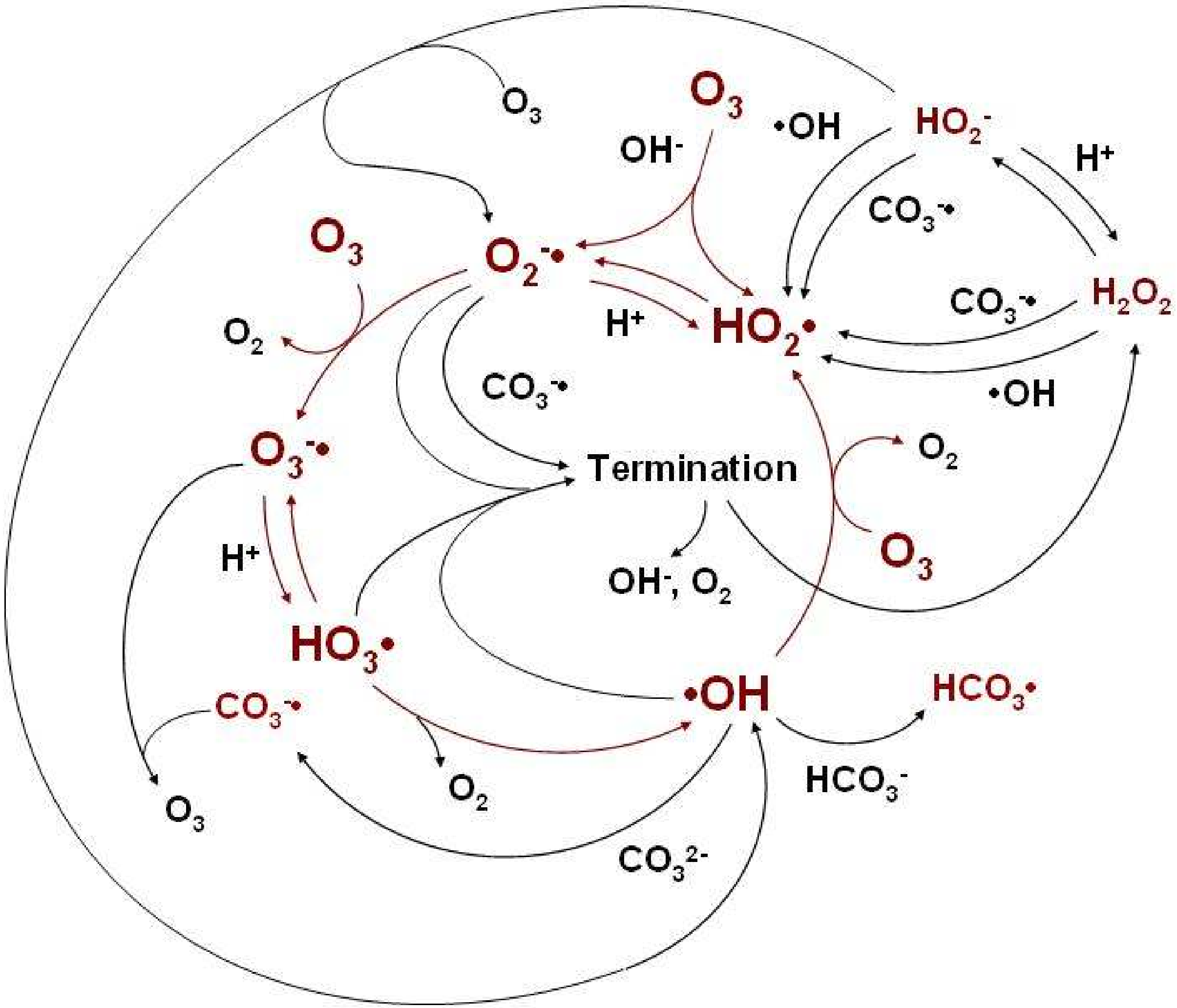


Table 2-3: Theoretical formation of hydroxyl radicals from the photolysis of ozone and hydrogen peroxide (Glaze et al., 1987).

	$\varepsilon_{254\ nm}$ in $M^{-1}\ cm^{-1}$	Stoichiometry	OH° formed per incident photon [a)]
H_2O_2	20	$H_2O_2 \rightarrow 2\ OH°$	0.09
O_3	3 300	$O_3 \rightarrow 2\ OH°$	2.00

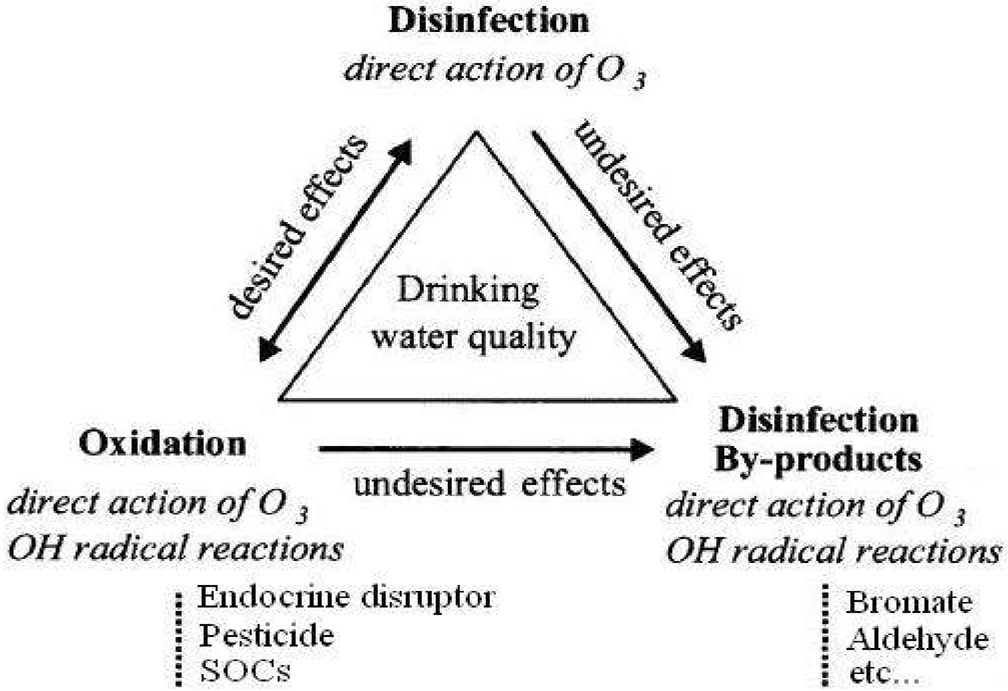
[a)] assumes 10 cm path length; $c(O_3) = c(H_2O_2) = 10^{-4}$ M

Mechanism of ozone decomposition



Application of ozone in water and waste water

- **Desired and undesired effect of ozonation processes**



Disinfection
direct action of O_3

desired effects

undesired effects

Drinking water quality

Oxidation
direct action of O_3
OH radical reactions

Endocrine disruptor
Pesticide
SOCs

undesired effects

Disinfection By-products
direct action of O_3
OH radical reactions

Bromate
Aldehyde
etc...

Disinfection and oxidation are the main goals for the application of ozone.

Both processes are accompanied by the undesired formation of disinfection by-products

Ozone oxidation

- **Oxidation of inorganic and organic compounds**

The kinetics of the reactions of ozone with inorganic and organic compounds is typically second order, first order in ozone and first order in the compound.

$$S + O_3 \rightarrow \text{Products}$$

$$-d[S]/dt = k[S][O_3]$$

For a batch-type or plug-flow reactor this yields:

$$\ln([S]/[S]_0) = -k \int [O_3]dt$$

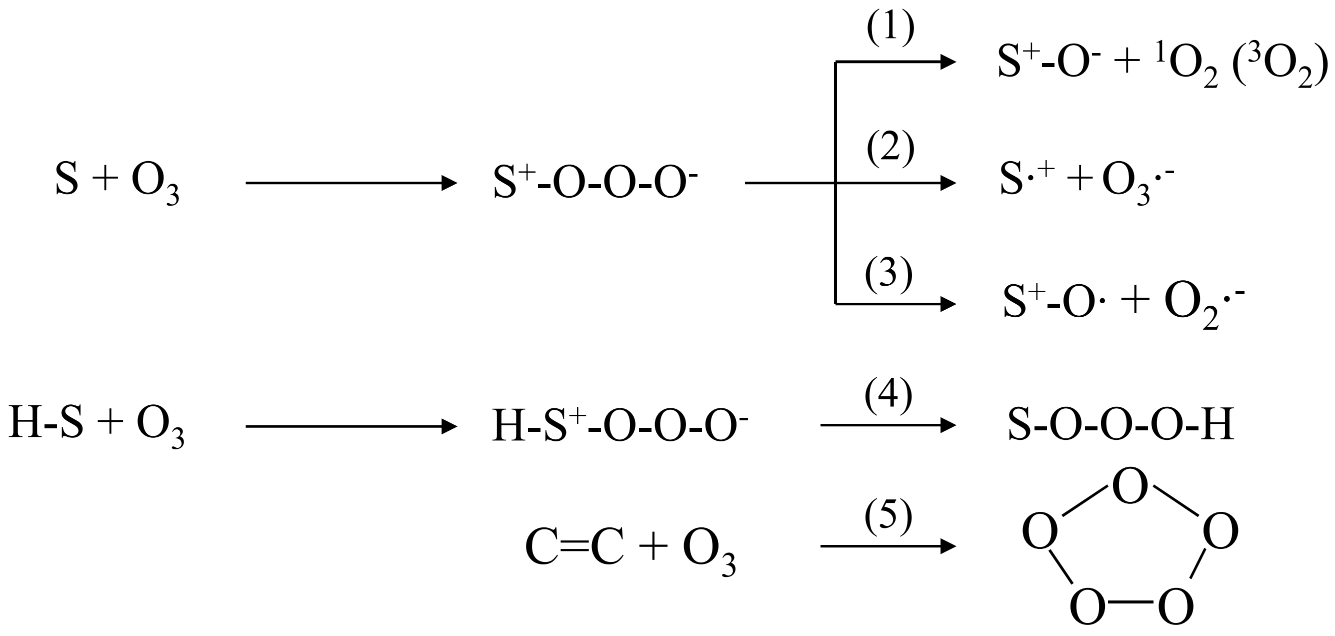
The ozonation time required to decrease the concentration of S to 50% of initial value becomes

$$t_{1/2} = 0.69 / (k[O_3])$$

Ozone oxidation

- **Kinetics of ozone reaction**

Primary reaction of ozone with a compound S



$$S + O_3 \longrightarrow S^{+}\text{-O-O-O}^{-}$$

$$S^{+}\text{-O-O-O}^{-} \xrightarrow{(1)} S^{+}\text{-O}^{-} + {}^{1}O_2\ ({}^{3}O_2)$$

$$S^{+}\text{-O-O-O}^{-} \xrightarrow{(2)} S^{\cdot +} + O_3^{\cdot -}$$

$$S^{+}\text{-O-O-O}^{-} \xrightarrow{(3)} S^{+}\text{-O}\cdot + O_2^{\cdot -}$$

$$H\text{-}S + O_3 \longrightarrow H\text{-}S^{+}\text{-O-O-O}^{-} \xrightarrow{(4)} S\text{-O-O-O-H}$$

$$C{=}C + O_3 \xrightarrow{(5)}$$

(1) Oxygen atom transfer to anionic, uncharged and cationic species

(2) Electron transfer (3) Formation of an oxyl radical

(4) Ozone insertion (5) Ring formation

2.1
Types of Molecular Ozone Reactions

O_3 reacts with reactants primarily with its end-standing electrophilic O-atoms. The most often described types of reactions of aqueous O_3 are:

a) *Electron-Transfer Reactions*

$$\underset{\textit{superoxide ion}}{O_2^{-}} + O_3 \longrightarrow O_2 + \underset{\textit{ozonide anion}}{O_3^{-}} \qquad (1)$$

$$\underset{\textit{hydroperoxide anion}}{HO_2^{-}} + O_3 \longrightarrow \underset{\textit{hydroperoxyl}}{HO_2^{\bullet}} + \underset{\textit{ozonide anion}}{O_3^{-}} \qquad (2)$$

2.1
Types of Molecular Ozone Reactions

b) *Oxygen-Atom Transfer Reactions*

$$OH^- + O_3 \longrightarrow HO_2^- + O_2 \quad (3)$$

hydroperoxide anion

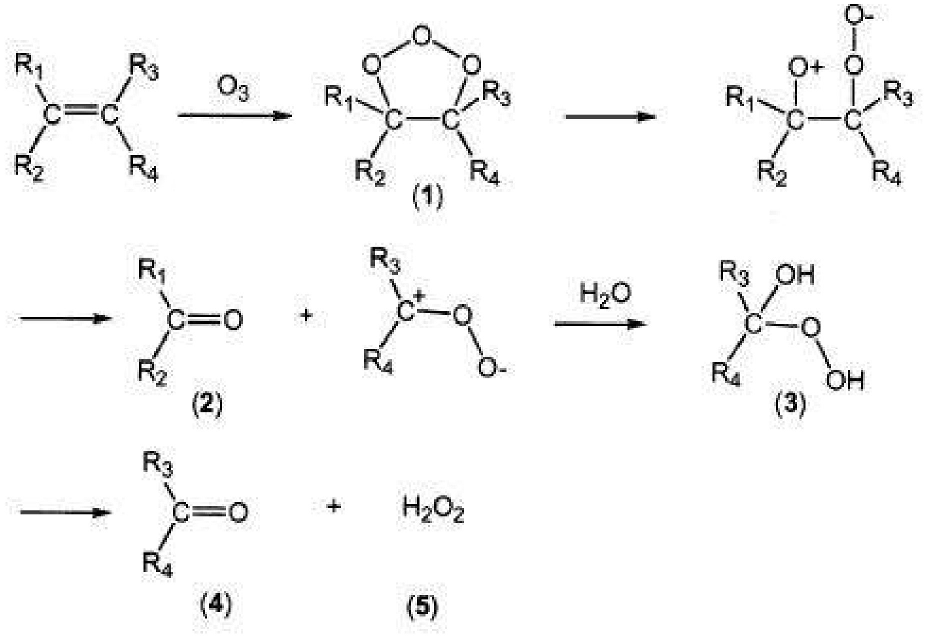
$$Fe^{2+} + O_3 \longrightarrow FeO^{+2} + O_2 \quad (4)$$

Fe^(IV)

$$NO_2^- + O_3 \longrightarrow NO_3^- + O_2 \quad (5)$$

Ozone oxidation

- **Reaction of olefines with ozone**



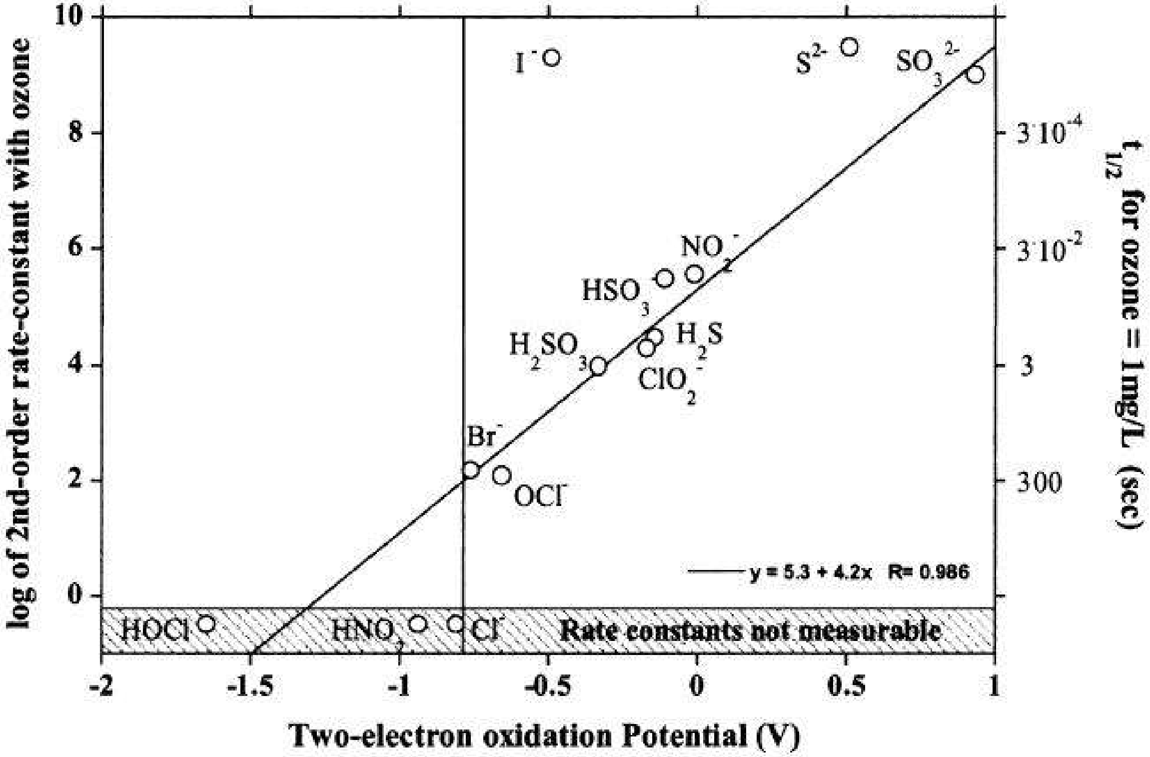
Initiation by the formation of an ozonide (1), an unstable cyclic trioxide

It decomposes into a carbonyl compound (2) and a hydroxyhydroperoxide (3)

This hydroxyhydroperoxide then slowly decomposes into a carbonyl compound (4) and hydrogen peroxide (5)

Ozone oxidation

- **Linear free energy relation between two electron oxidation potential and the rate constant by ozone**



- the rate constants over 7 orders of magnitude
- protonation of a species decreases the rate of oxidation due to a decrease in nucleophilicity
- iodide ➔ a different mechanism ?

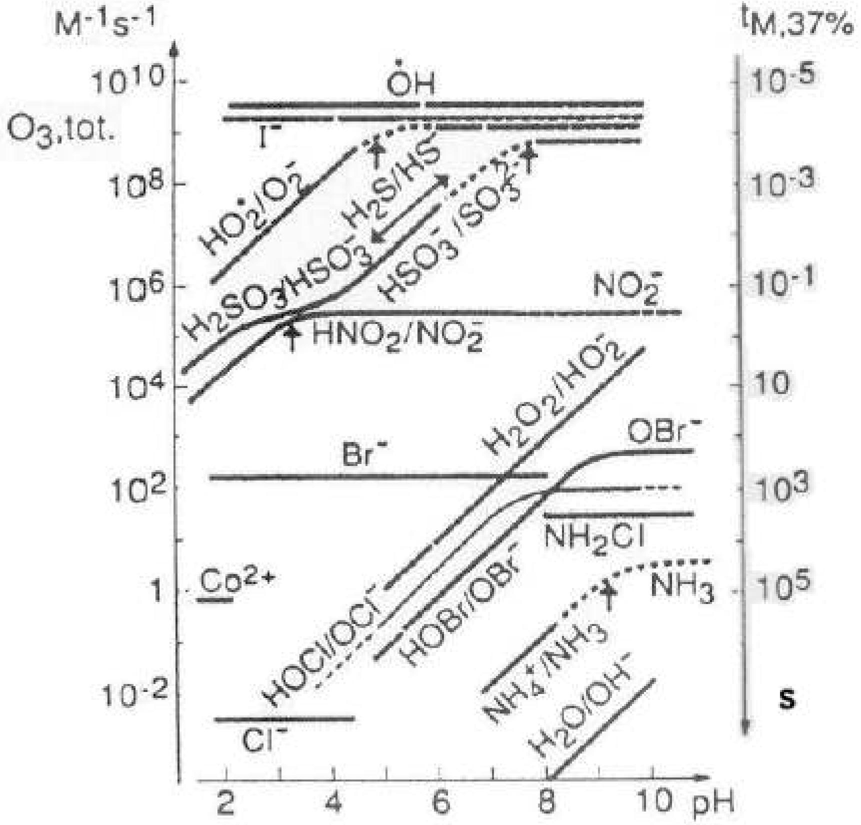


Fig. 4. Examples for aqueous second-order rate constants k_M for direct reactions of ozone with inorganic solutes as a function of pH (cf. Eq. (10). Right-hand scale: $t_{M,37\%}$ is the reaction time (τ) required to reduce the concentration of the indicated solute by a factor e (i.e. to 37%) (cf. Eq. 14). Vertical arrows indicate pK_a values. *Assumptions:* $[O_3]$ = 10 μM (0.5 mg/l); no interferences by secondary oxidants; batch-type or plug-flow reactor. Data from [28], Fig. adapted from [20]

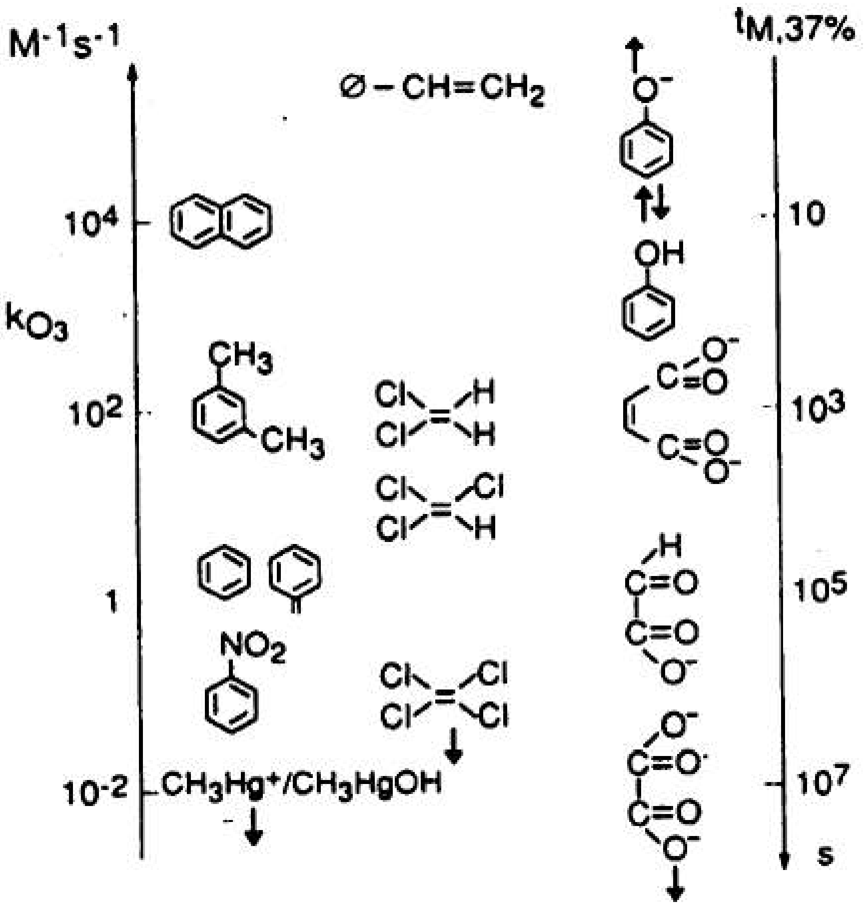


Fig. 5. Examples for aqueous second-order rate constants k_M for direct reactions of ozone with non-dissociating organic solutes (cf. Eq. (10). Right-hand scale: $t_{M,37\%}$ is the reaction time (τ) required to reduce the concentration of the indicated solute by a factor e (i.e. to 37%) (cf. Eq. 14). Assumptions as for Fig. 4. Data from [27], Fig. adapted from [20]

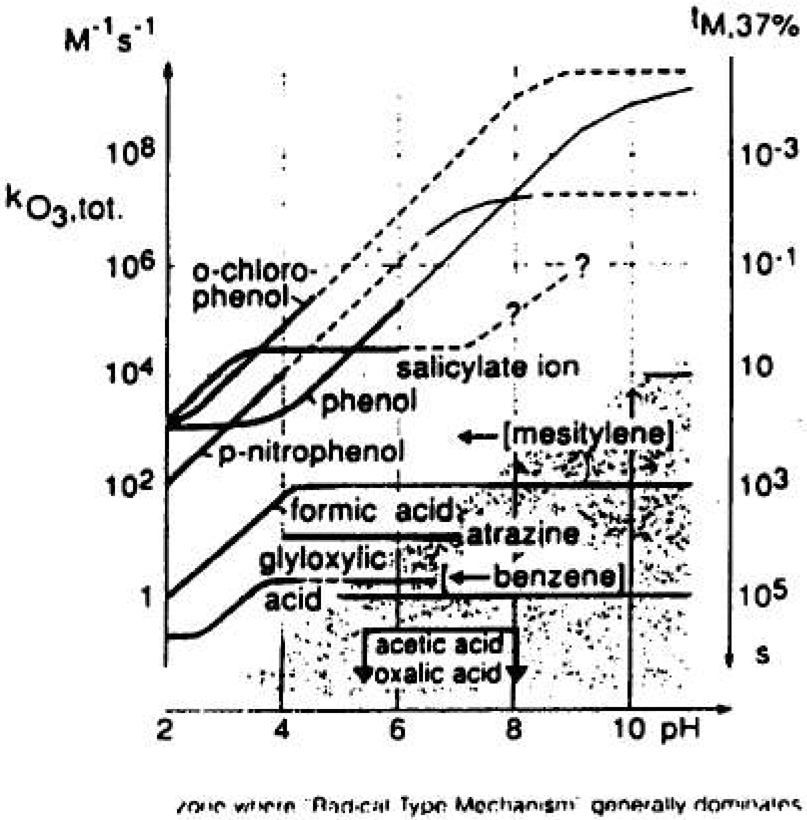
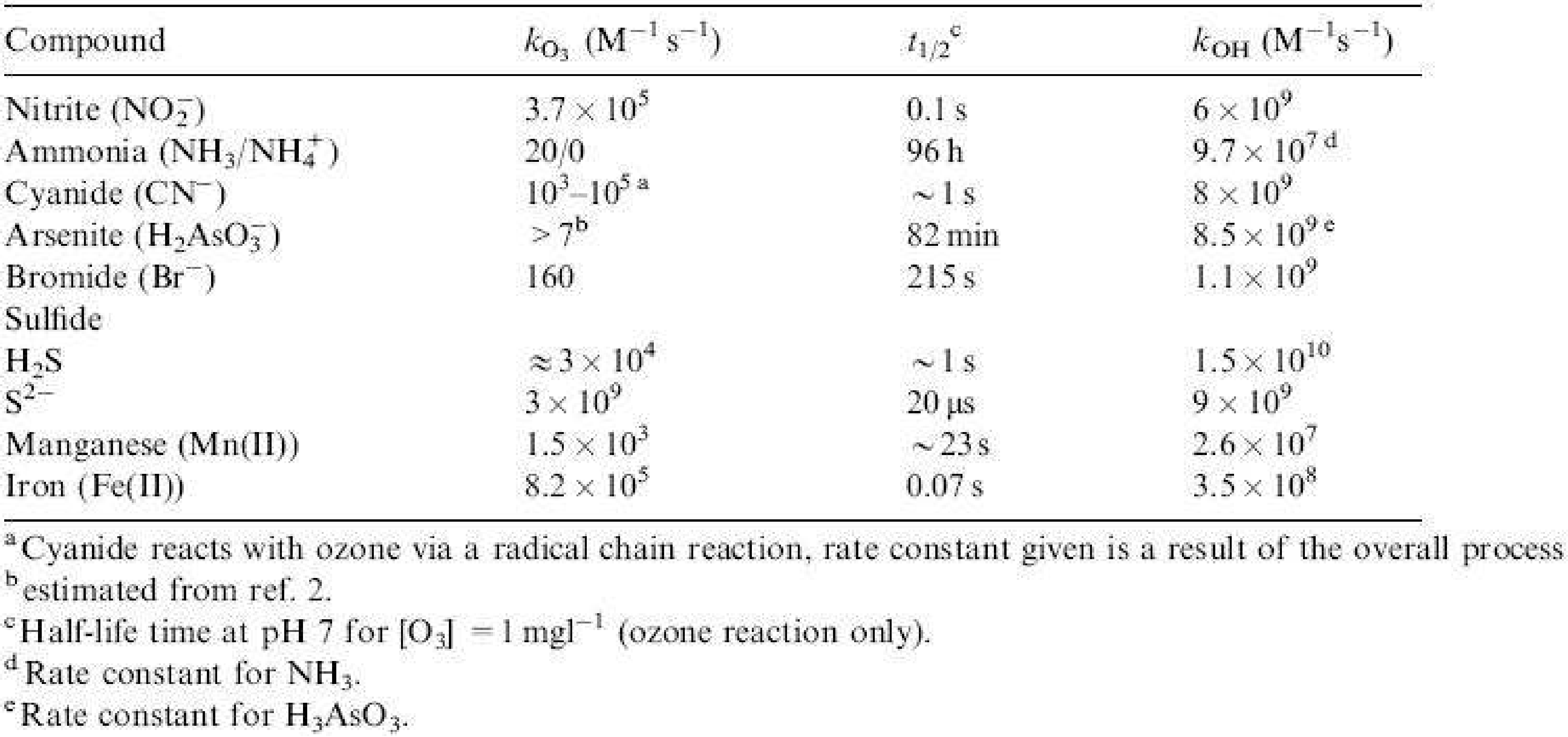


Fig. 6. Examples for aqueous second-order rate constants k_M for direct reactions of ozone with dissociating organic solutes as a function of pH (cf. Eq. (10). Right-hand scale: $t_{M,37\%}$ is the reaction time (τ) required to reduce the concentration of the indicated solute by a factor e (i.e. to 37%) (cf. Eq. 14). Assumptions as for Fig. 4. Data from [27], Fig. adapted from [20]

Ozone oxidation

- **Kinetics of inorganic compounds with ozone and ·OH**



Compound	k_{O_3} ($M^{-1}s^{-1}$)	$t_{1/2}$[c]	k_{OH} ($M^{-1}s^{-1}$)
Nitrite (NO_2^-)	3.7×10^5	0.1 s	6×10^9
Ammonia (NH_3/NH_4^+)	20/0	96 h	9.7×10^7 [d]
Cyanide (CN^-)	10^3–10^5 [a]	~1 s	8×10^9
Arsenite ($H_2AsO_3^-$)	> 7[b]	82 min	8.5×10^9 [e]
Bromide (Br^-)	160	215 s	1.1×10^9
Sulfide			
H_2S	$\approx 3 \times 10^4$	~1 s	1.5×10^{10}
S^{2-}	3×10^9	20 µs	9×10^9
Manganese (Mn(II))	1.5×10^3	~23 s	2.6×10^7
Iron (Fe(II))	8.2×10^5	0.07 s	3.5×10^8

[a] Cyanide reacts with ozone via a radical chain reaction, rate constant given is a result of the overall process

[b] estimated from ref. 2.

[c] Half-life time at pH 7 for $[O_3] = 1\ mgl^{-1}$ (ozone reaction only).

[d] Rate constant for NH_3.

[e] Rate constant for H_3AsO_3.

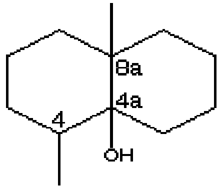
In the case of short half-lives ($t_{1/2} < 5$ min), ozonation is very efficient for the transformation of a compounds because it occurs mainly via the direct ozone reaction

For slower processes, OH radicals play an important role

Ozone oxidation

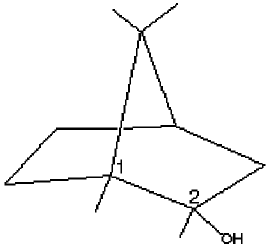
- **Kinetics of organic compounds with ozone and ·OH**

Compound	k_{O_3} ($M^{-1} s^{-1}$)	$t_{1/2}$[c]	k_{OH} ($M^{-1} s^{-1}$)
Algal products			
Geosmin	$<10^a$	> 1 h	8.2×10^9
2-Methylisoborneol (MIB)	$<10^a$	> 1 h	$\approx 3 \times 10^9$
Mycrocystin-LR	3.4×10^4	1 s	



Geosmin

Earthy-musty taste and odor compounds such as Geosmin and MIB are difficult to oxidize with ozone, because they consist of saturated ring systems.

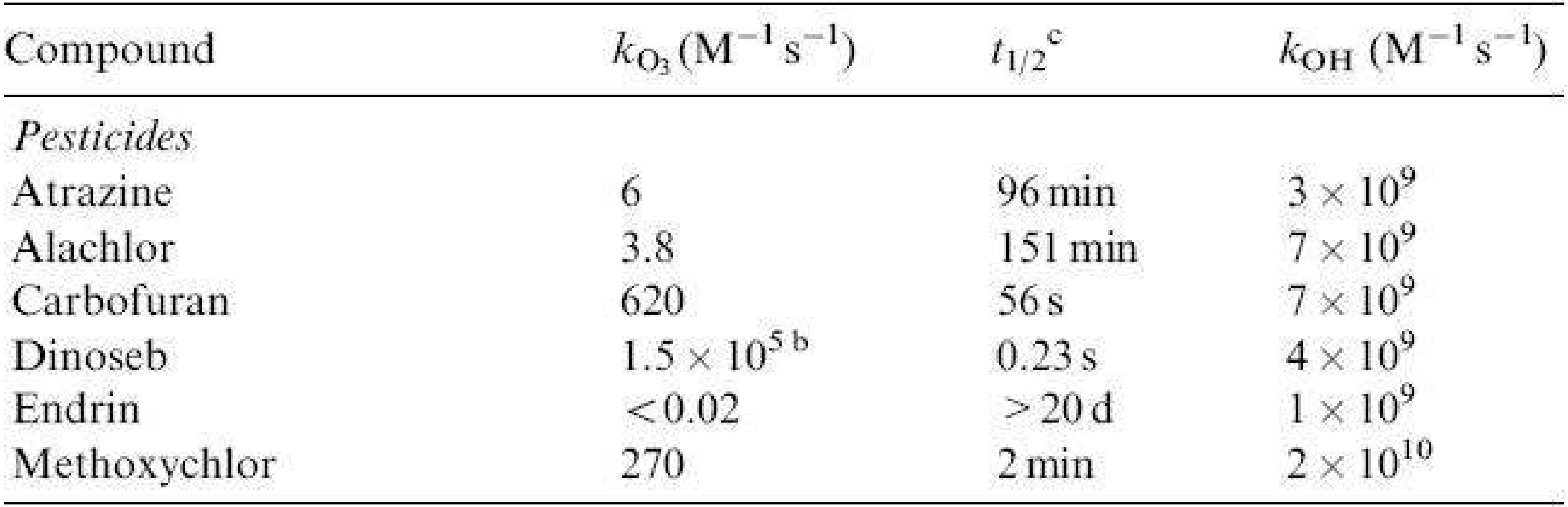


MIB

Since these compounds have high rate constants for the oxidation by OH radicals, AOP (O_3 / H_2O_2) is well suited for their oxidation. Only partial oxidation of the compounds is necessary to eliminate taste and odor problems.

Ozone oxidation

- **Kinetics of organic compounds with ozone and ·OH**



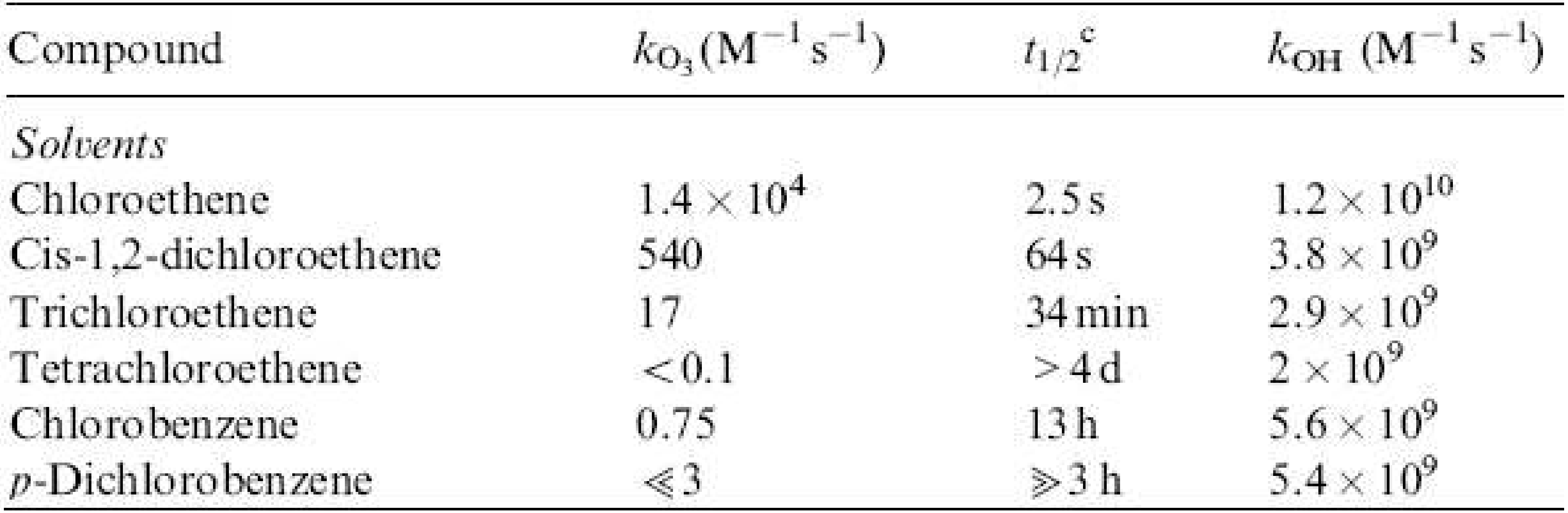
Compound	k_{O_3} ($M^{-1}s^{-1}$)	$t_{1/2}{}^{c}$	k_{OH} ($M^{-1}s^{-1}$)
Pesticides			
Atrazine	6	96 min	3×10^9
Alachlor	3.8	151 min	7×10^9
Carbofuran	620	56 s	7×10^9
Dinoseb	$1.5 \times 10^{5\,b}$	0.23 s	4×10^9
Endrin	< 0.02	> 20 d	1×10^9
Methoxychlor	270	2 min	2×10^{10}

The rate constants for the oxidation of pesticides with ozone cover a range of more than five orders of magnitude. The lowest reactivity is observed for endrin, a cyclic compound with a chloro substituted double bond.

These electron-withdrawing groups lead to the low reactivity.

Ozone oxidation

- **Kinetics of organic compounds with ozone and ·OH**



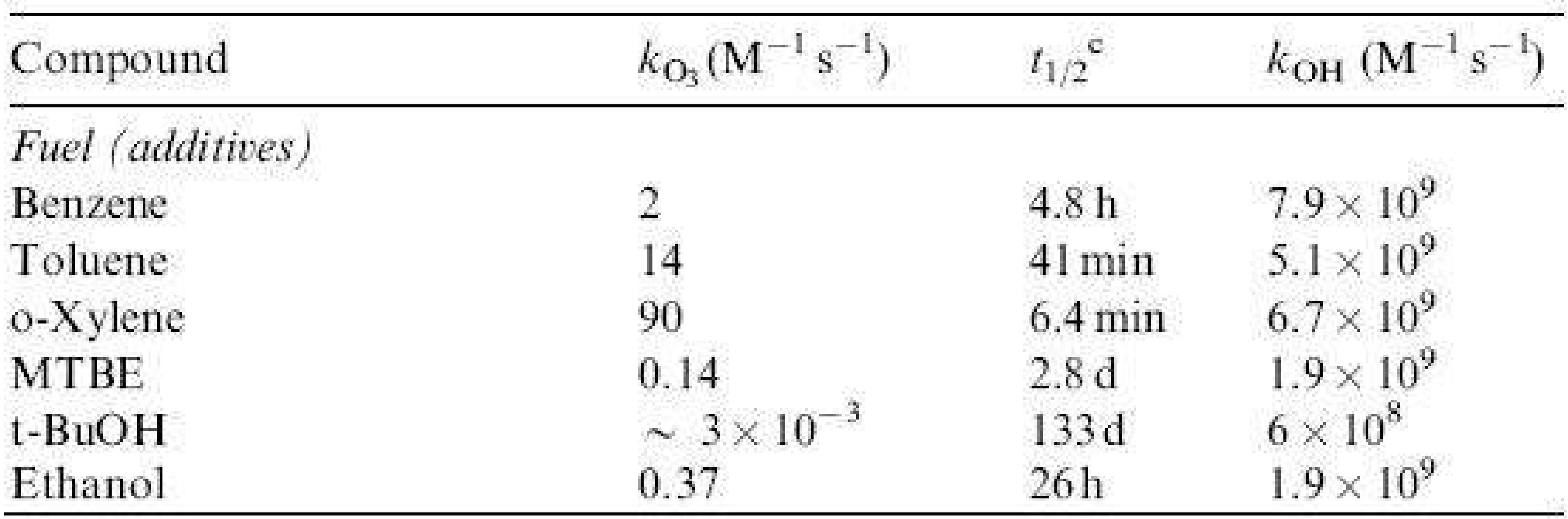
Compound	k_{O_3} ($M^{-1}s^{-1}$)	$t_{1/2}{}^{c}$	k_{OH} ($M^{-1}s^{-1}$)
Solvents			
Chloroethene	1.4×10^4	2.5 s	1.2×10^{10}
Cis-1,2-dichloroethene	540	64 s	3.8×10^9
Trichloroethene	17	34 min	2.9×10^9
Tetrachloroethene	<0.1	>4 d	2×10^9
Chlorobenzene	0.75	13 h	5.6×10^9
p-Dichlorobenzene	$\leqslant 3$	$\geqslant 3$ h	5.4×10^9

The second-order rate constant for the reaction of olefines with ozone decreases by a factor of ≥ 10 for each additional chlorine substituent.

The reactivity of tri-and tetrachloroethene with ozone is substantially lower and especially in the case of tetrachloroethene, the oxidation is governed by OH radicals

Ozone oxidation

- **Kinetics of organic compounds with ozone and ·OH**

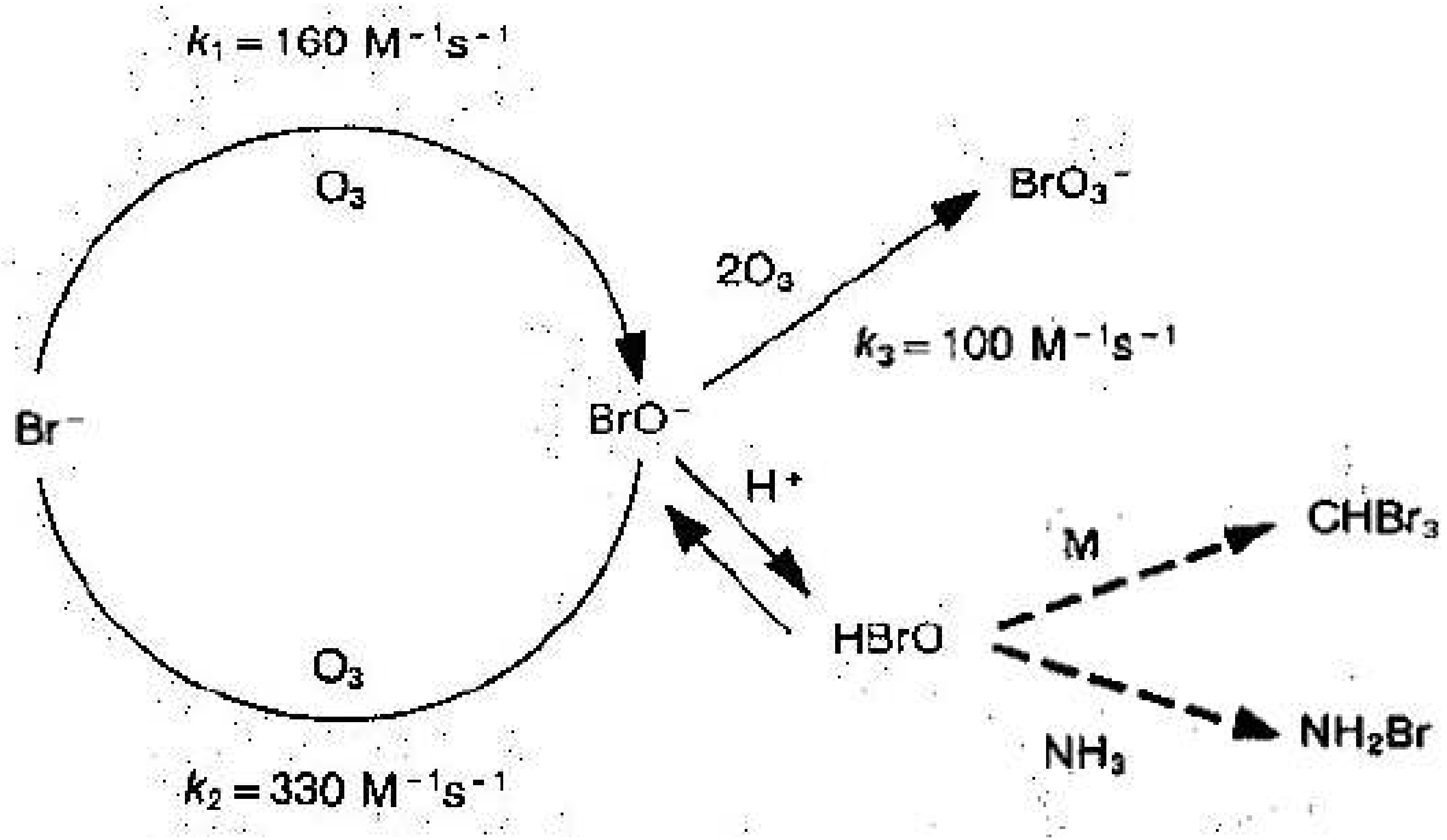


Compound	k_{O_3} ($M^{-1} s^{-1}$)	$t_{1/2}{}^{c}$	k_{OH} ($M^{-1} s^{-1}$)
Fuel (additives)			
Benzene	2	4.8 h	7.9×10^9
Toluene	14	41 min	5.1×10^9
o-Xylene	90	6.4 min	6.7×10^9
MTBE	0.14	2.8 d	1.9×10^9
t-BuOH	$\sim 3 \times 10^{-3}$	133 d	6×10^8
Ethanol	0.37	26 h	1.9×10^9

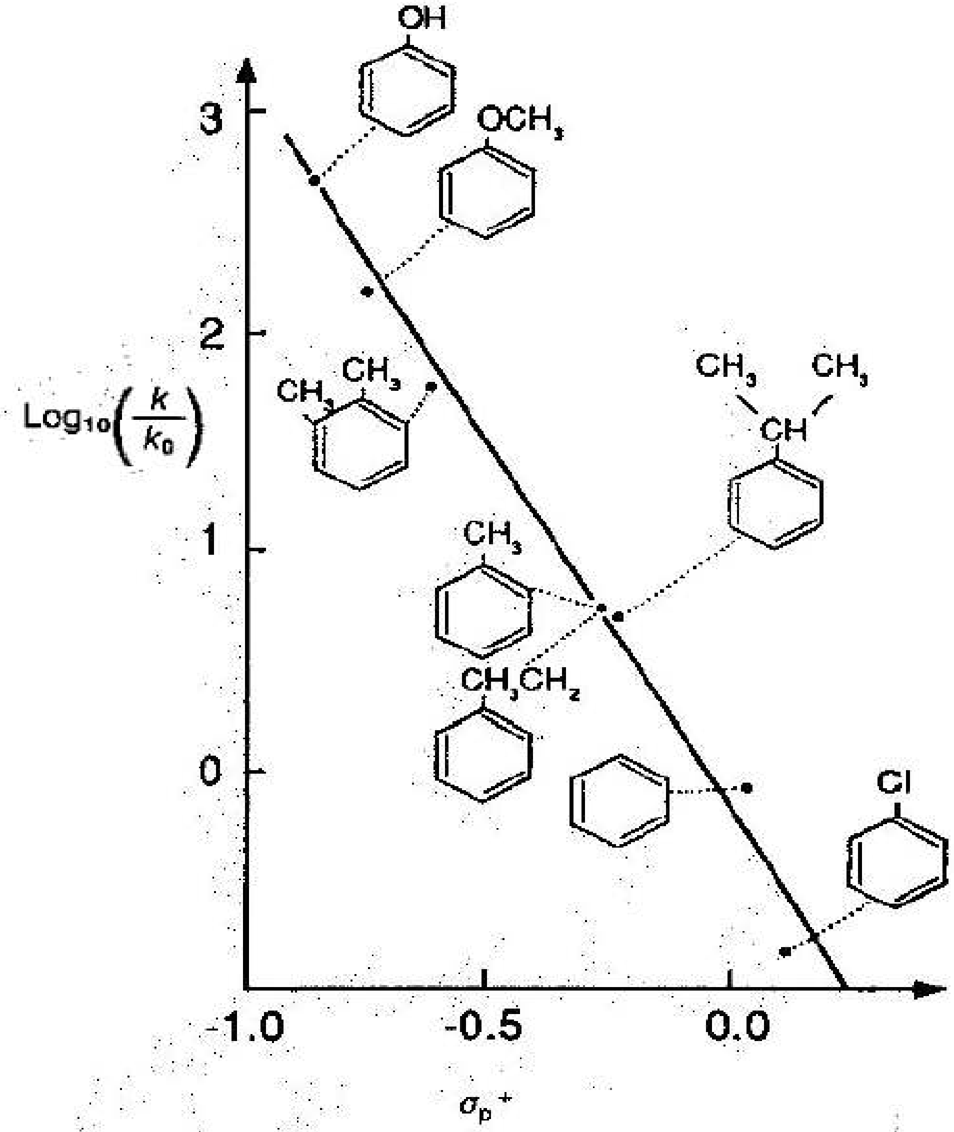
The reactivity of benzene, toluene, ehylbenzene and xylene with ozone increases with the degree of substitution with methyl group.

This fast reaction means that the reaction of ozone with aromatic ring system is highly electrophilic and also highly selective. Electron donor groups on the aromatic ring lead to an enhanced rate, whereas electron-withdrawing groups cause a slower
Rate.

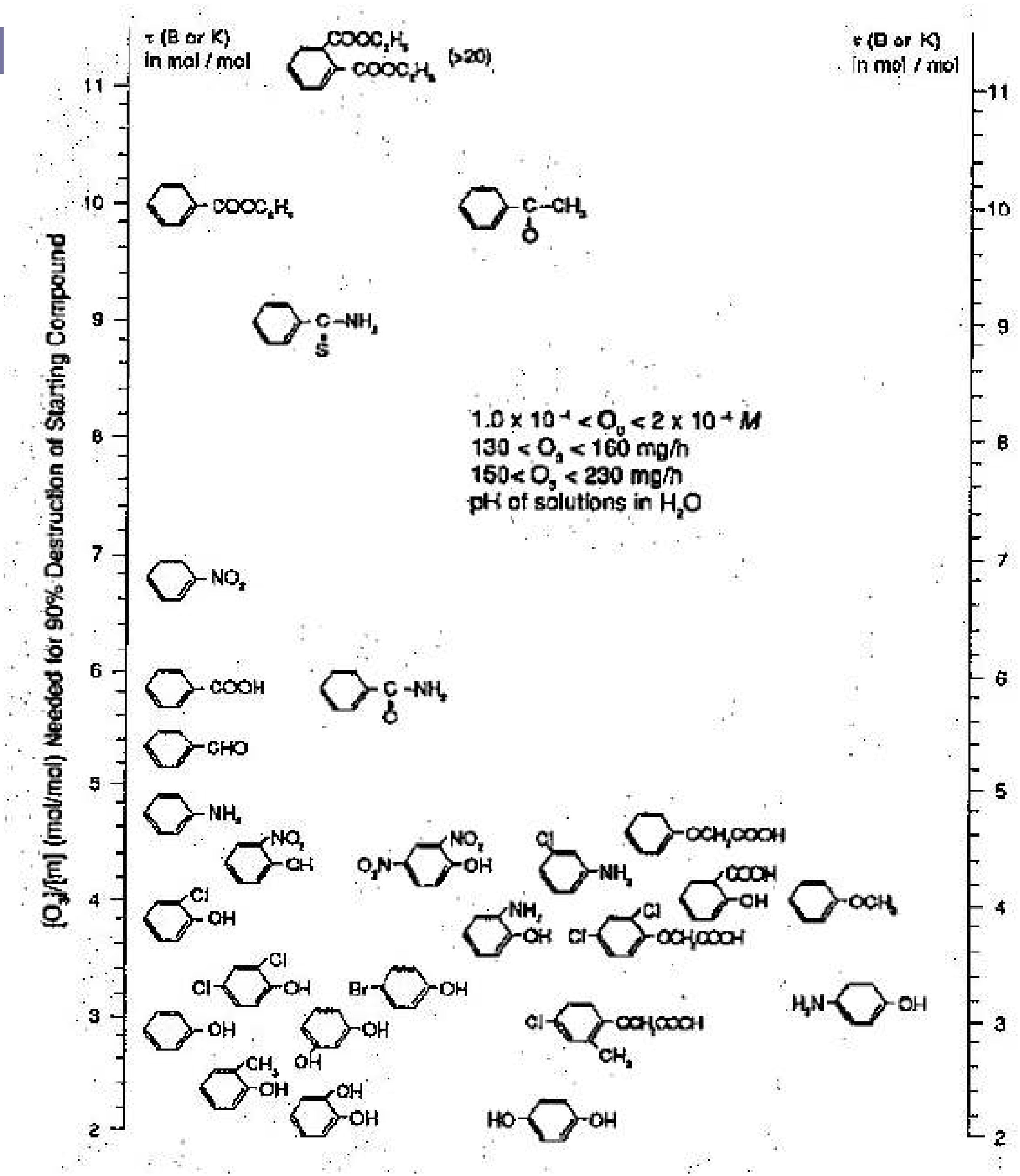
Diagram of Bromide Oxidation Cycle



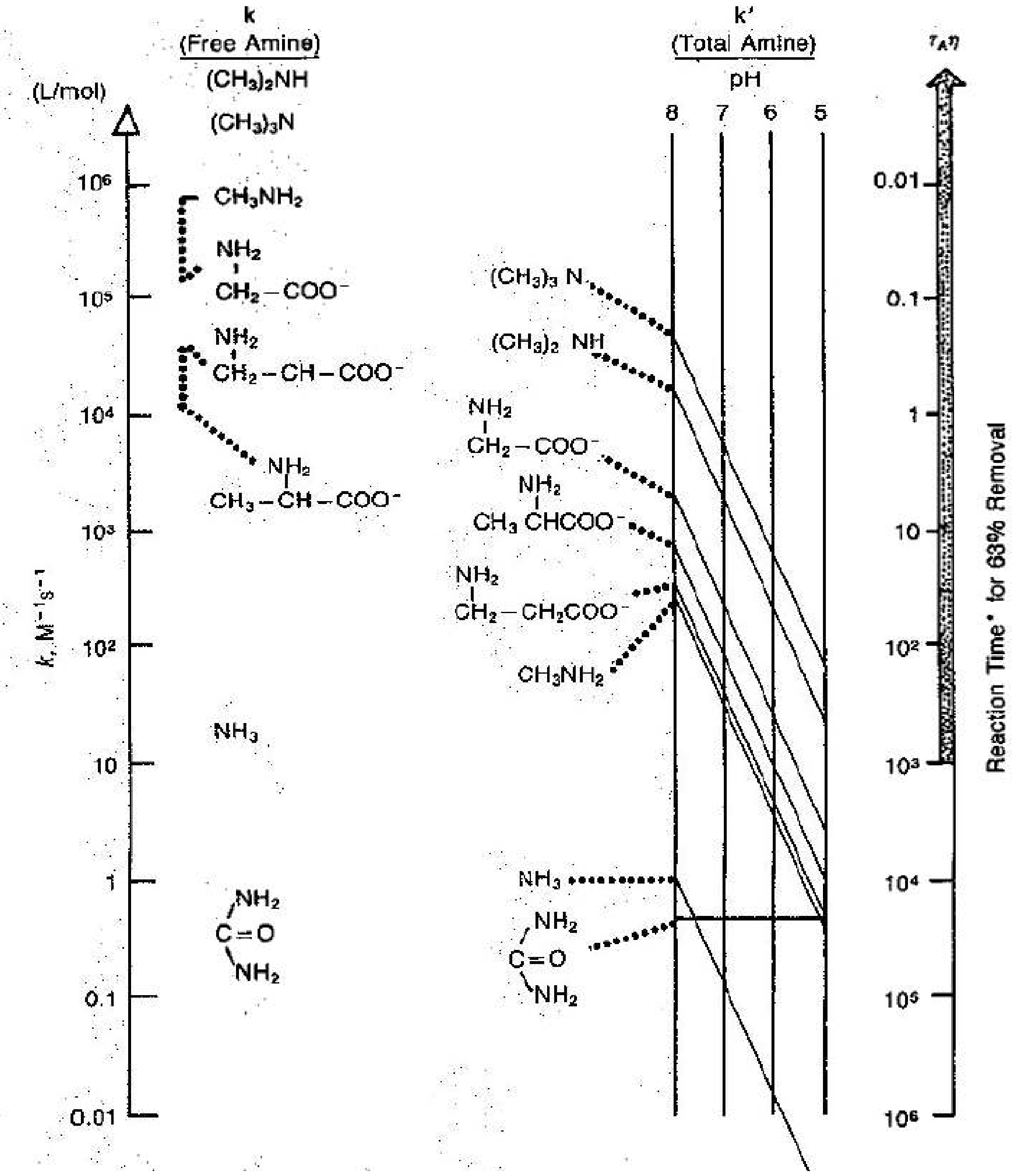
Stock–Brown Plot of Ko Values of Substituted Benzenes



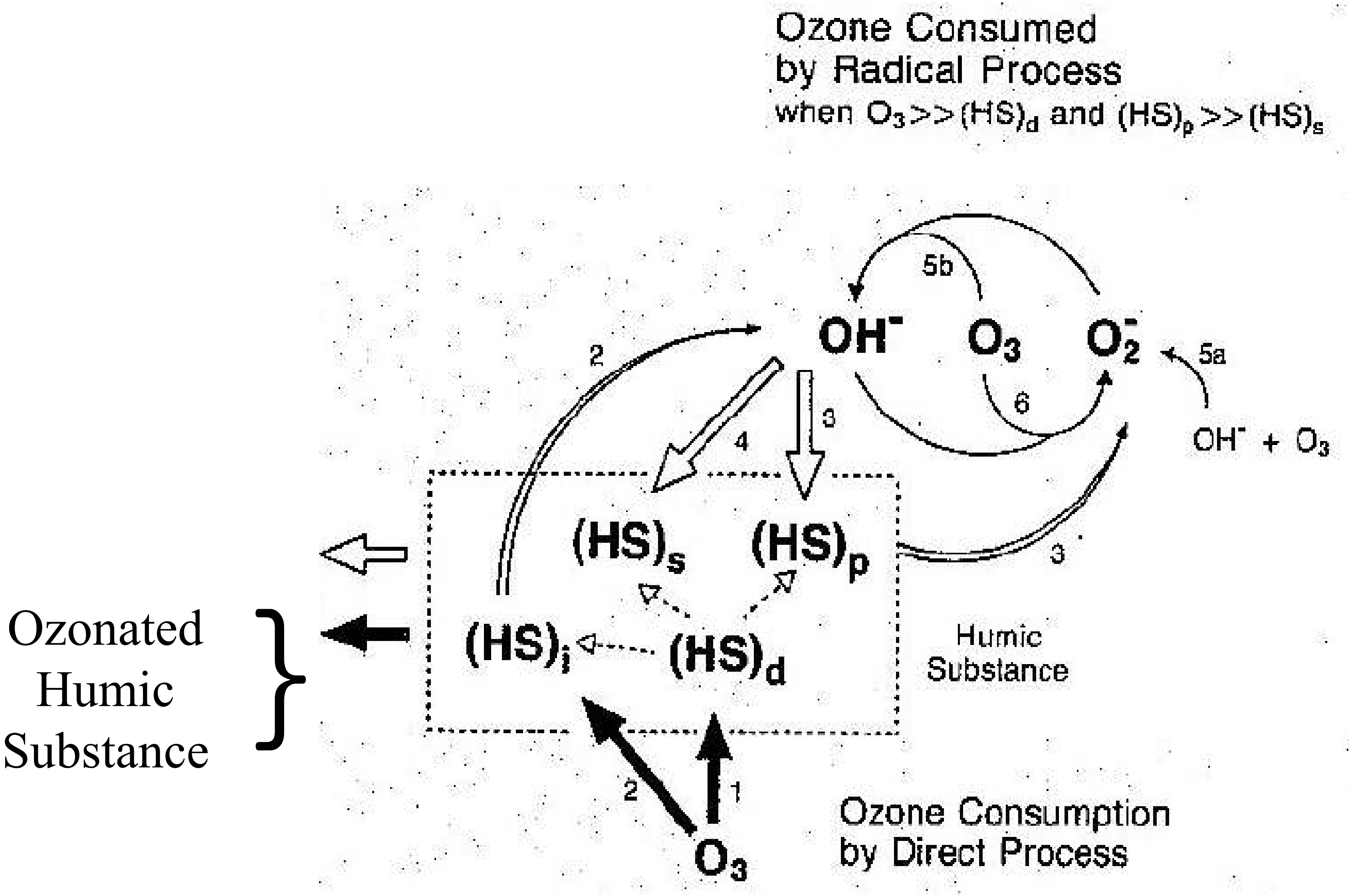
Ozone Dosage Needed to Obtain 90 Percent Aromatic Clearance



Rate Constants for Amine - Ozone Reaction



Ozone Action on Humic Substances Containing Several Reactive Sites



Ozonated
Humic
Substance

Scheme of Competition for reaction with ·OH

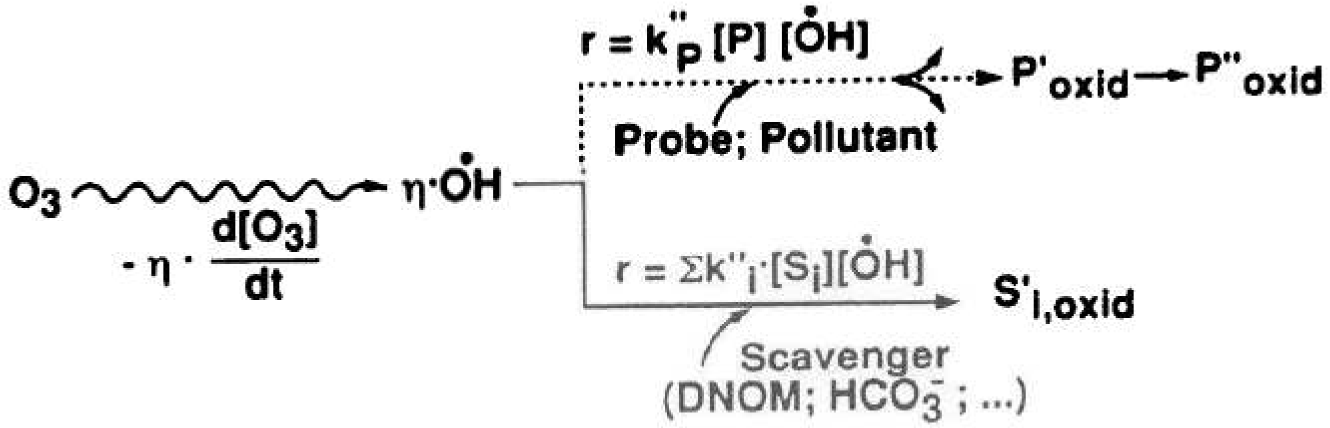


Fig. 12. Scheme of competition for reaction with OH radicals. A trace compound P (probe or pollutant) is highly protected by the sum of further OH radical scavengers S

$$-\frac{d[P]}{dt}=\eta\frac{d[\Delta O_3]}{dt}\frac{k_p[P]}{\sum(k_{OH,s}[S_i])}=\frac{d[\Delta O_3][P]}{dt\Omega_P}$$

$$\ln\frac{[P]_t}{[P]_0}=-\frac{\Delta O_3}{\Omega_P}$$

$$=(\sum(k_{OH,S}[S_i]))/(\eta\cdot k_{OH,P})$$

$(\Delta O_3)_{37\%,P}$: the amount of O_3 required to reduced the concentration P to 37% of the initial value independent of P concentration

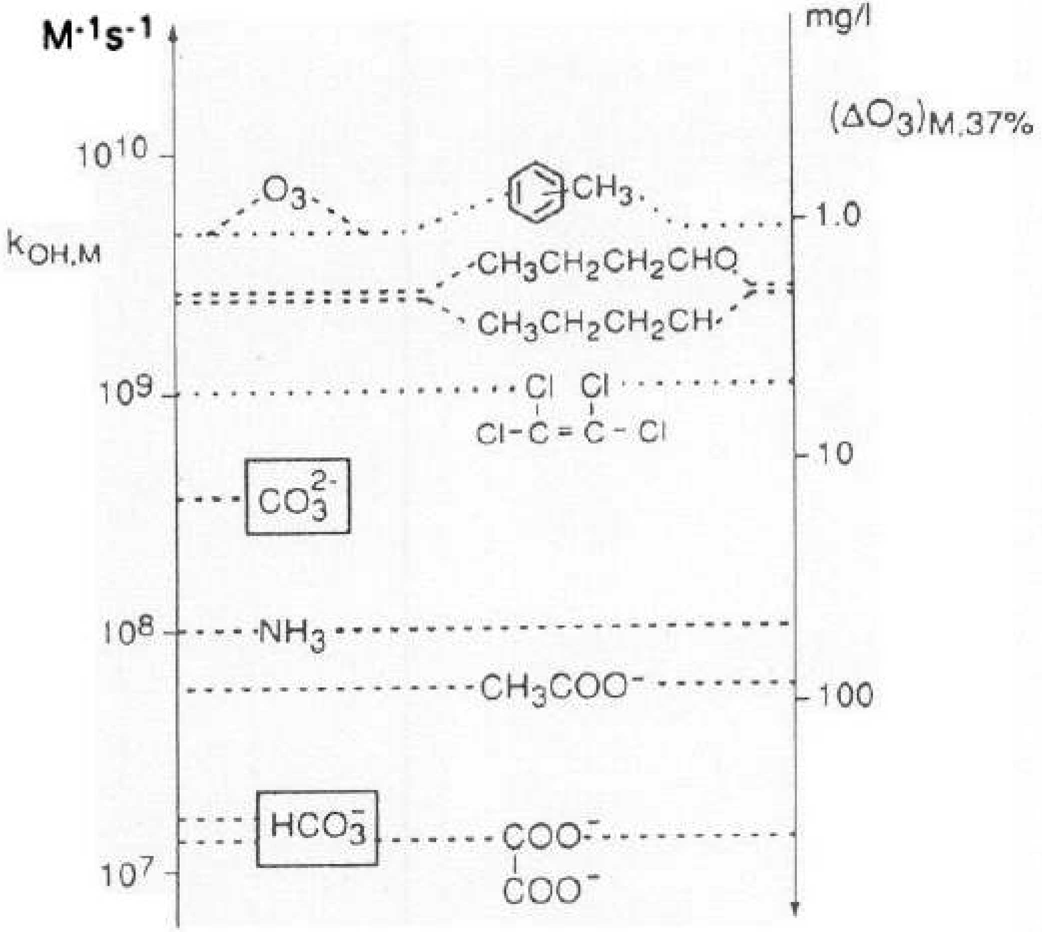


Fig. 11. Examples for aqueous second-order rate constants $k_{OH,M}$ for reactions of $OH^{\cdot}$ with different solutes M (cf. Eq. (18). Right-hand scale: $(\Delta O_3)_{M,37\%}$ is the dosage of ozone to be transformed into $OH^{\cdot}$ to decrease the concentration of the indicated substrate compound M to 37% of its primary concentration. This scale is calibrated for ozonation of a eutrophic lakewater (DOC = 4 mg/l), $[HCO_3^-] = 1.6$ mM, pH = 8.3). *Assumptions:* $\eta = 0.5$; batch-type or plug-flow reactor. Adapted from [20]

$$(\Delta O_3)_{37\%,P} = (\Sigma(k_{OH,S}\ [S_i]))/(\eta \cdot k_{OH,P})$$

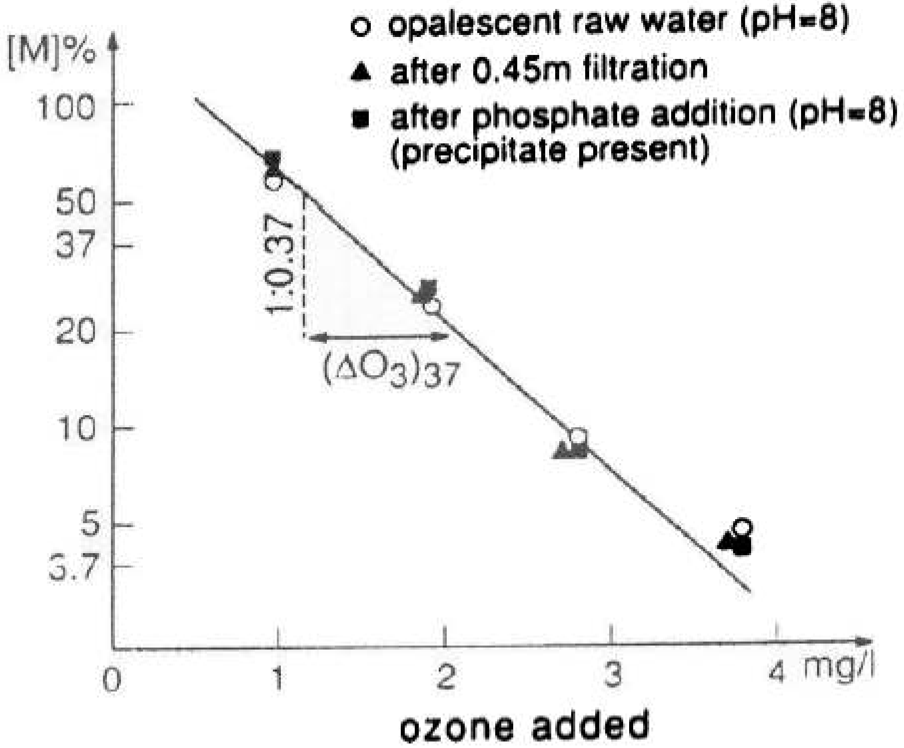


Fig. 13. Elimination of an ozone-resistant organic micropollutant M (benzene) which was spiked as a probe to samples of water from eutrophic Lake Greifensee (DOC = 3.6 mg/l; $[HCO_3^-]$ = 1.9 mM; pH = 8). The reaction has been shown to be only controlled by OH radical reactions [45]. (For large series of comparable measurements also see references given in [53])

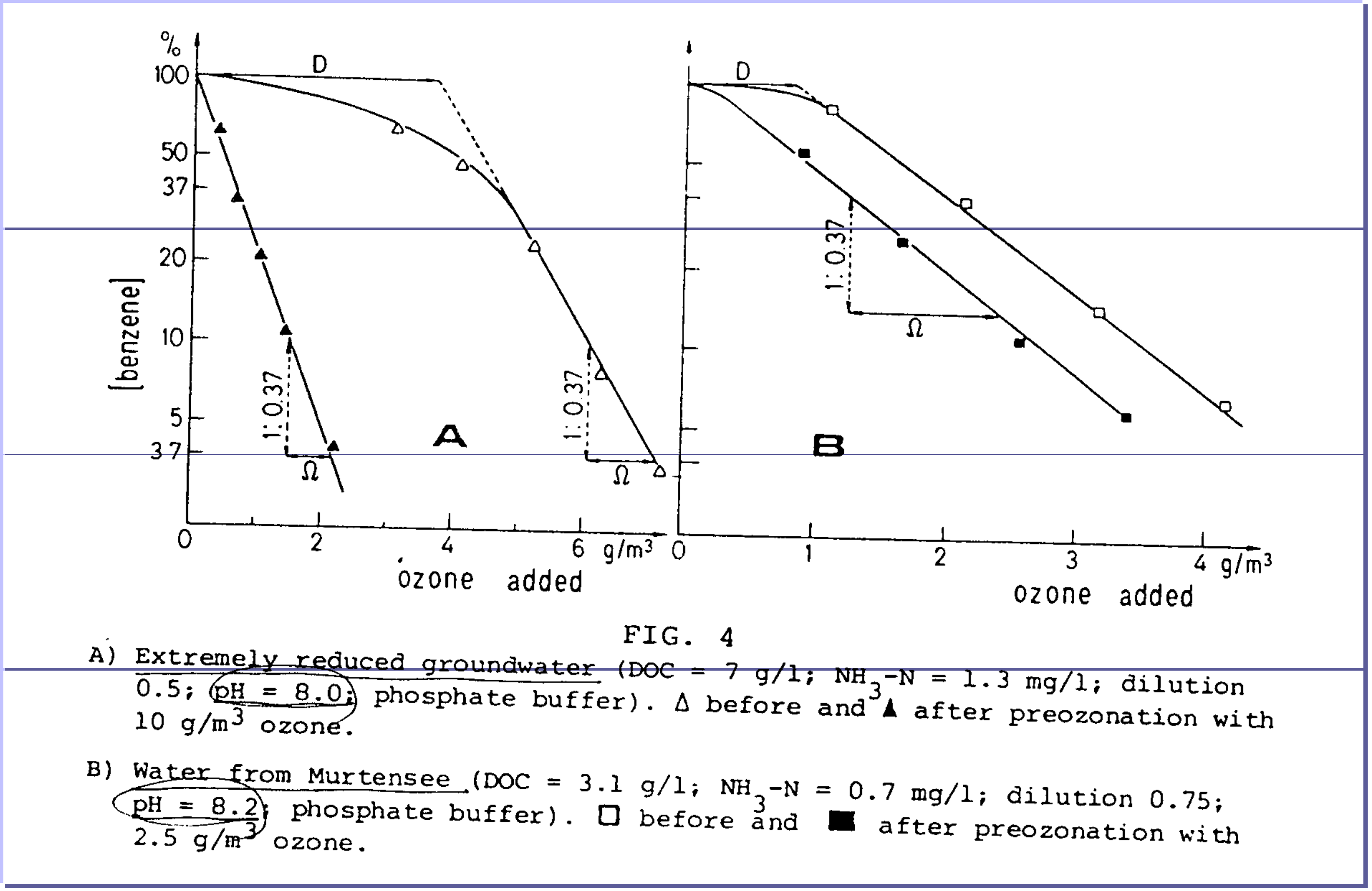


FIG. 4

A) Extremely reduced groundwater (DOC = 7 g/l; NH_3-N = 1.3 mg/l; dilution 0.5; pH = 8.0; phosphate buffer). Δ before and ▲ after preozonation with 10 g/m^3 ozone.

B) Water from Murtensee (DOC = 3.1 g/l; NH_3-N = 0.7 mg/l; dilution 0.75; pH = 8.2; phosphate buffer). □ before and ■ after preozonation with 2.5 g/m^3 ozone.

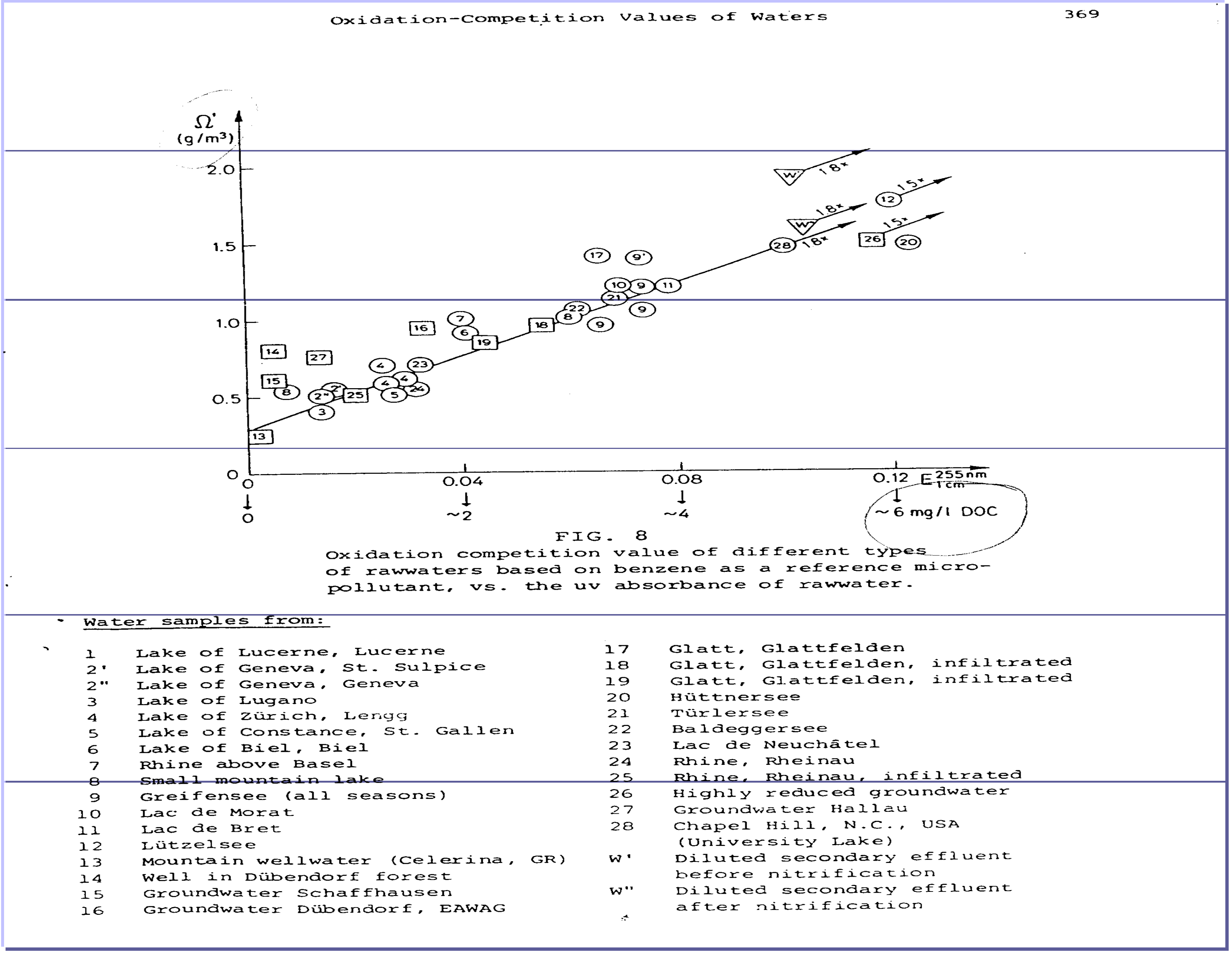


FIG. 8
Oxidation competition value of different types of rawwaters based on benzene as a reference micro-pollutant, vs. the uv absorbance of rawwater.

Water samples from:

1	Lake of Lucerne, Lucerne
2'	Lake of Geneva, St. Sulpice
2"	Lake of Geneva, Geneva
3	Lake of Lugano
4	Lake of Zürich, Lengg
5	Lake of Constance, St. Gallen
6	Lake of Biel, Biel
7	Rhine above Basel
8	Small mountain lake
9	Greifensee (all seasons)
10	Lac de Morat
11	Lac de Bret
12	Lützelsee
13	Mountain wellwater (Celerina, GR)
14	Well in Dübendorf forest
15	Groundwater Schaffhausen
16	Groundwater Dübendorf, EAWAG
17	Glatt, Glattfelden
18	Glatt, Glattfelden, infiltrated
19	Glatt, Glattfelden, infiltrated
20	Hüttnersee
21	Türlersee
22	Baldeggersee
23	Lac de Neuchâtel
24	Rhine, Rheinau
25	Rhine, Rheinau, infiltrated
26	Highly reduced groundwater
27	Groundwater Hallau
28	Chapel Hill, N.C., USA (University Lake)
W'	Diluted secondary effluent before nitrification
W"	Diluted secondary effluent after nitrification

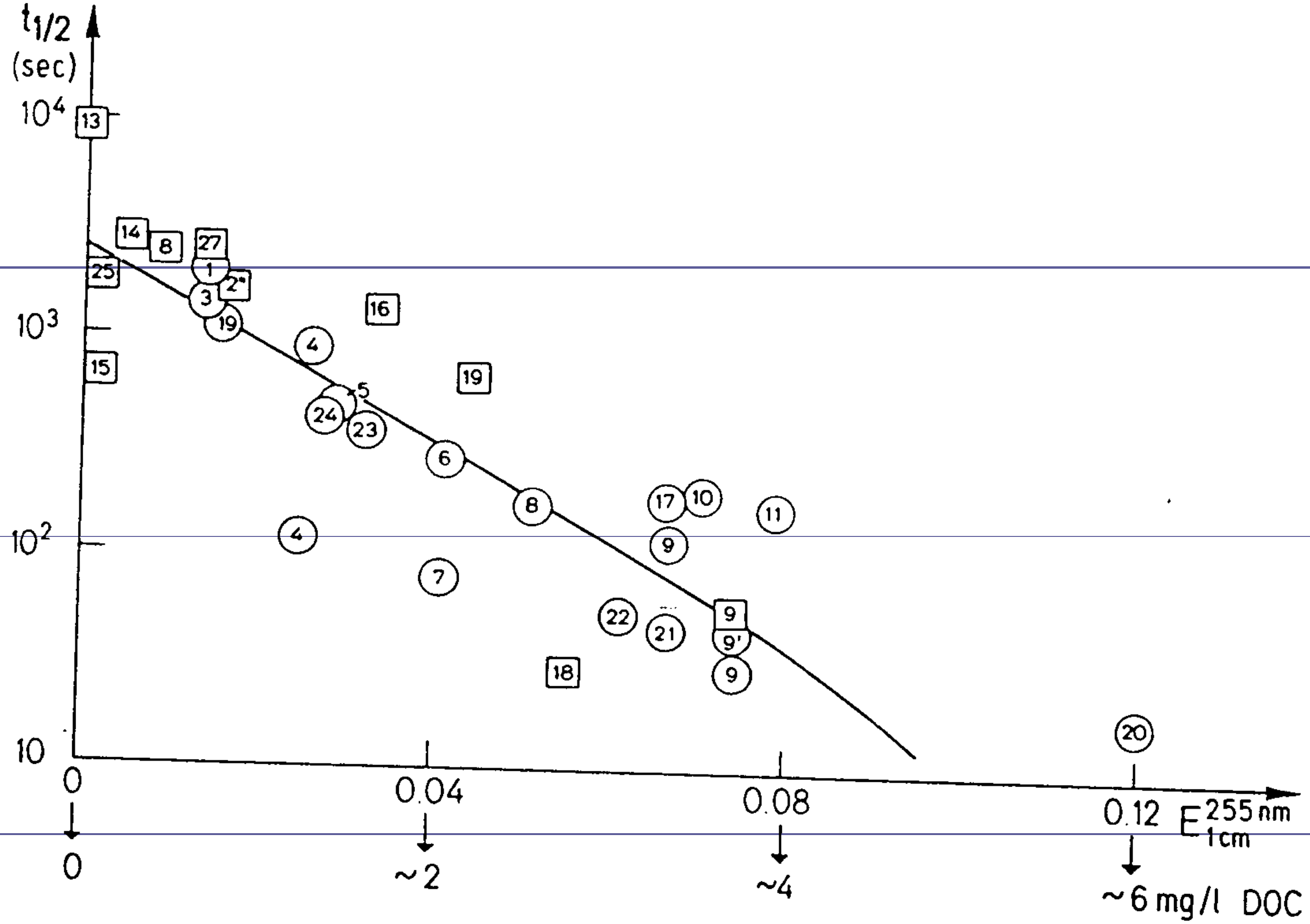


FIG. 9

Lifetime of ozone in typical drinking waters. $t_{1/2}$ is the time within the concentration of ozone drops from 50 % to 25 %, when its initial concentration is $10 g/m^3$. Generally the order of the decomposition changes with proceeding ozonation and $t_{1/2}$ therefore only gives a crude but helpful information (for legend of waters see FIG. 8).

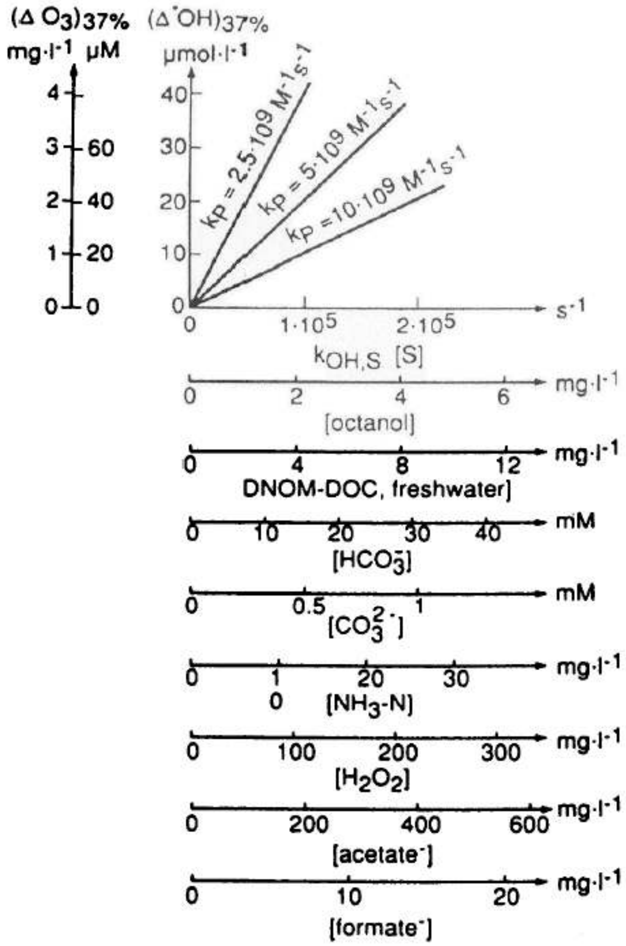


Fig. 14. $(\Delta O_3)_{37\%}$ and corresponding $(OH^\bullet)_{37\%}$ values required to eliminate pollutants P that react with $OH^\bullet$ with different reaction-rate constants to 37 % of the preceeding concentration. The values are plotted vs the rate constant with which $OH^\bullet$ become consumed by $OH^\bullet$ scavengers. The series of abscissa compare the concentration effects of different types of scavenging solutes. Extracted from Fig. 1, Ref. [53]

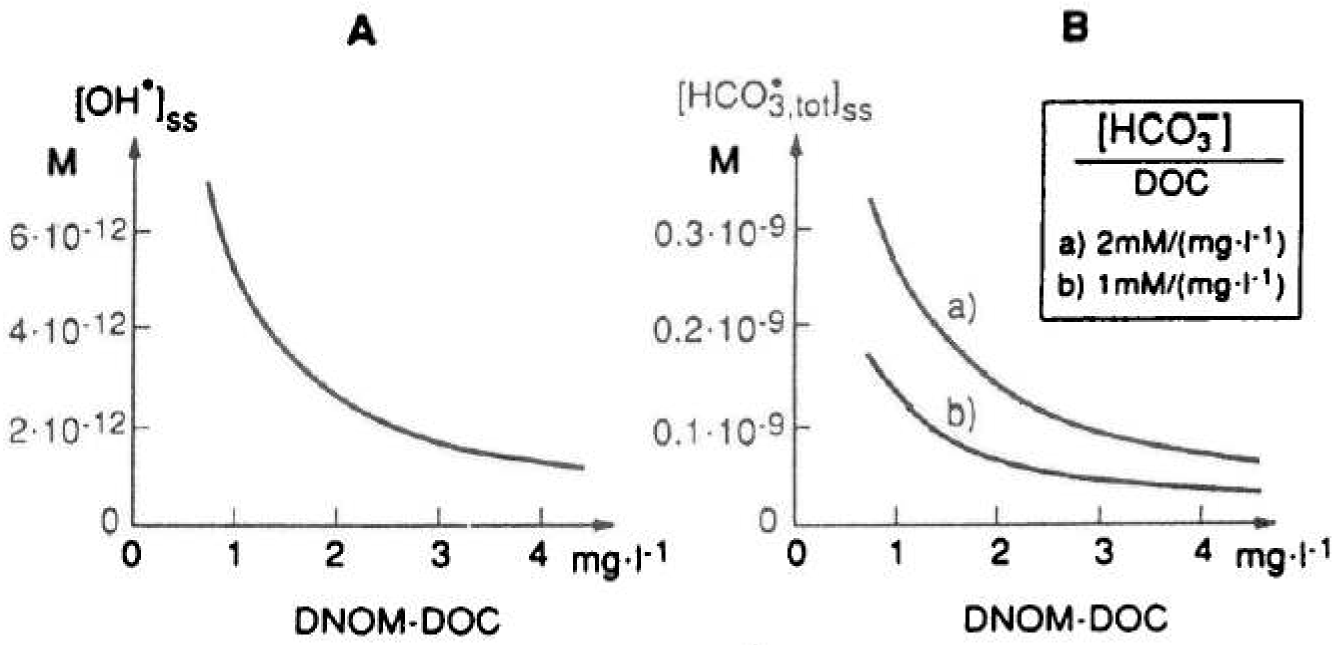


Fig. 15. Steady-state concentrations of $OH^{\cdot}$ and $HCO_3^{\cdot}/CO_3^{\cdot -}$ that occur in a water as a function of DOC.

Assumptions: A: 2.4 mg/l O_3 are transformed within 100 s (i.e. 0.5 μM · s^{-1}) to produce $OH^{\cdot}$ with a yieldfactor of 0.5; $OH^{\cdot}$-scavenging rate-coefficient from Fig. 14. B: As for A, and: half of the $OH^{\cdot}$ produced react with HCO_3^- to produce $HCO_3^{\cdot}/CO_3^{\cdot -}$; $HCO_3^{\cdot}/CO_3^{\cdot -}$-scavenging rate-coefficient are from Fig. 16

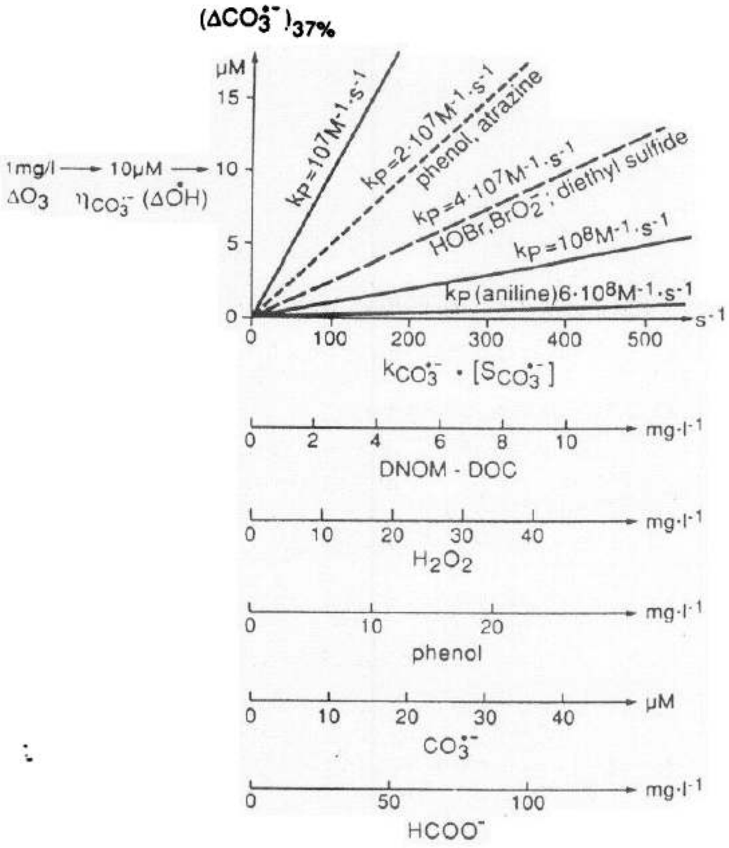


Fig. 16. $(CO_3^{\bullet-})_{37\%}$ required to eliminate pollutants P that **react** with different reaction-rate constants to 37% of the preceeding concentration. The values are plotted vs the rate constant with which $HCO_3^{\bullet}/CO_3^{\bullet-}$ become scavenged. The series of abscissa compares the concentration effects of different solutes acting as $HCO_3^{\bullet}/CO_3^{\bullet-}$ scavengers. The rate constants are from Ref. [14], except for DNOM-DOC and formate ion ($HCOO^-$) that are from [25] and [70], respectively

Ozone oxidation

- **Quantification of the oxidation by ozone and by OH radicals**

The oxidation of a micropollutant S during an ozonation process can be formulated as follows:

$$-d[S]/dt = k_{ozone}\,[S][O_3] + k_{OH}\,[S][\cdot OH]$$

The ratio R_{ct} of the concentrations of ozone and OH radicals can be measured by adding an ozone-resistant probe compound (e.g. pCBA)

$$R_{ct} = [\cdot OH] / [O_3]$$

$$-d[S]/dt = (k_{ozone} + k_{OH}\,R_{ct})\,[S][O_3]$$

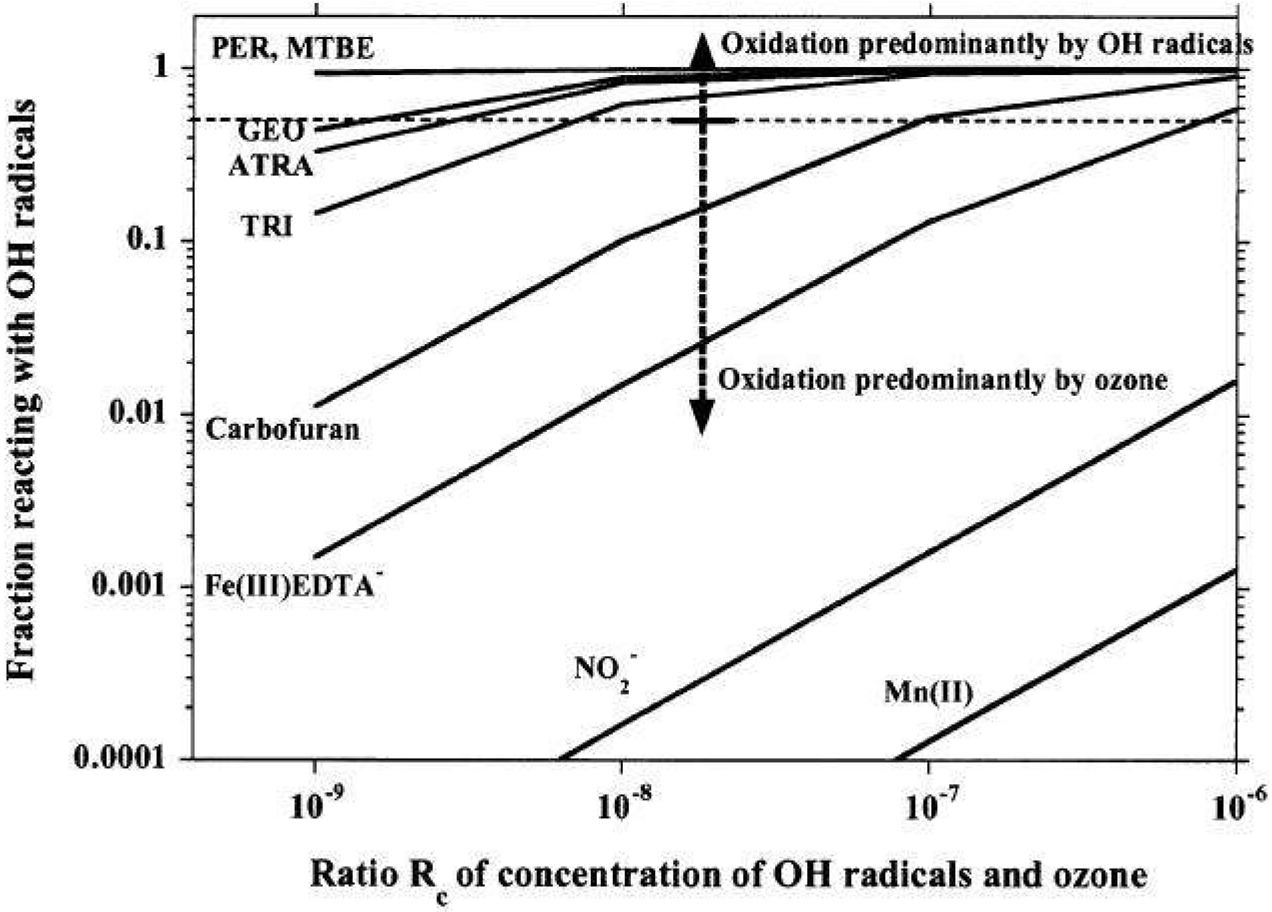
$$\mathrm{Ln}\,([S]/[S]_0) = -(k_{ozone} + k_{OH}\,R_{ct}) \int [O_3]dt$$

The fraction f_{OH} of S reacting with OH radicals can be calculated as

$$f\,([\cdot OH]) = k_{OH}\,R_{ct} / (k_{ozone} + k_{OH}\,R_{ct})$$

Ozone oxidation

- **Quantification of oxidation by ozone and by OH radicals**

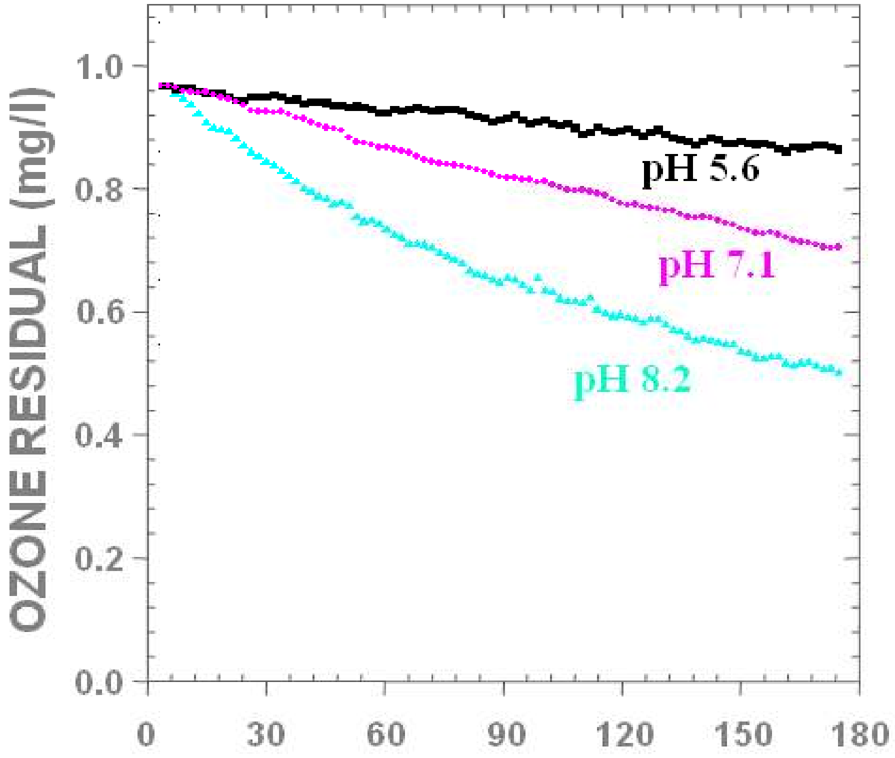


Fraction of compounds by OH radicals for a typical range of R_c values in natural waters

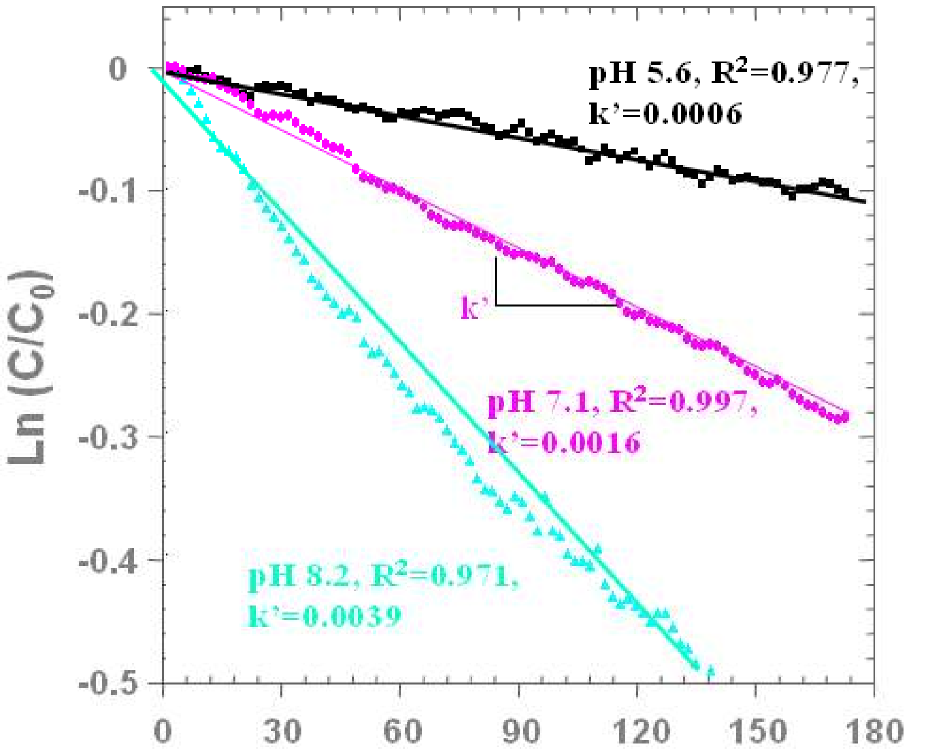
Mechanism of ozone decomposition

- **Ozone decomposition – buffer solution (FIA Assay)**

1. OZONE RESIDUAL

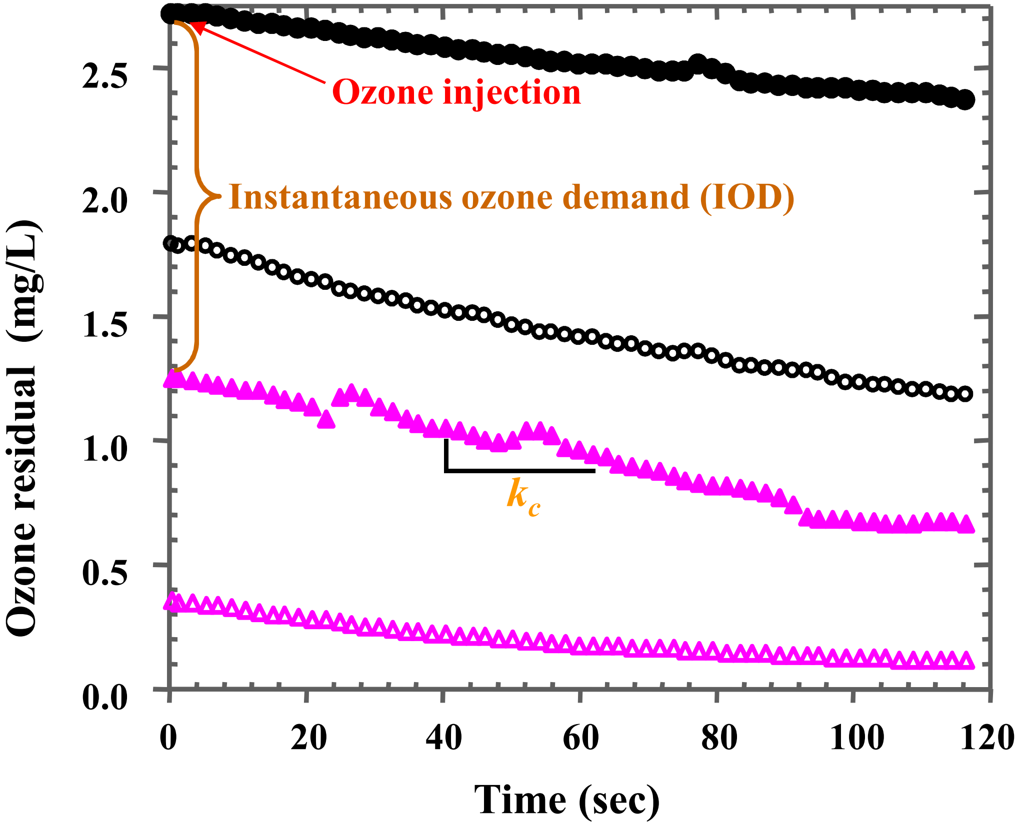


2. FIRST-ORDER OZONE DECAY



Mechanism of ozone decomposition

- Ozone decomposition – Raw water (FIA Assay)



● **Distilled water**
IOD = 0 mg/l

○ **Han River**
IOD = 0.9 mg/l

▲ **Suwannee River**
IOD = 1.45 mg/l

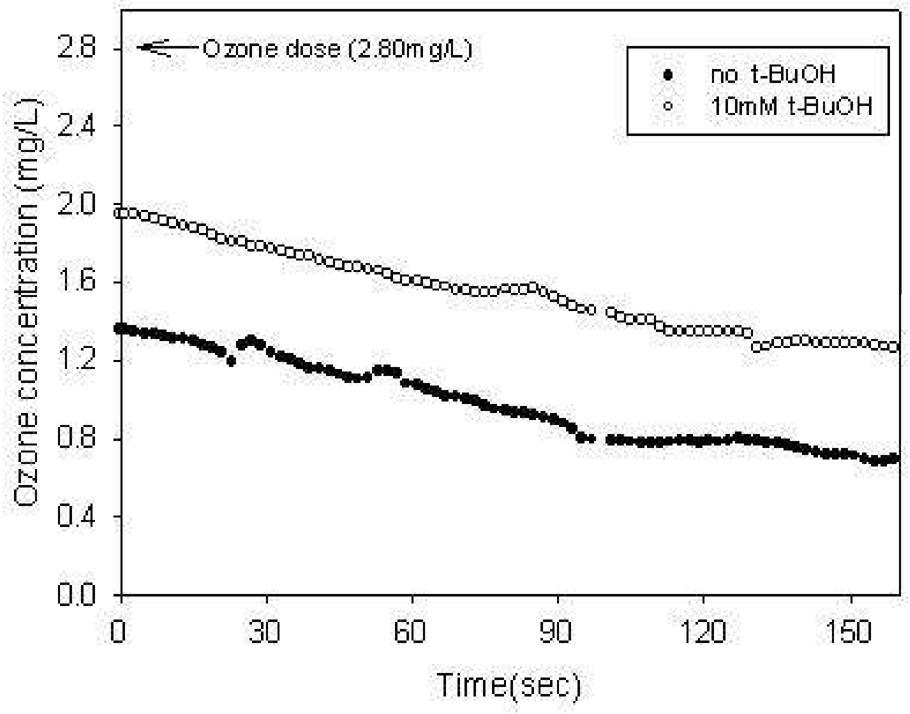
△ **Aldrich Humic**
IOD = 2.35 mg/l

Initial ozone : 2.7 mg/l
pH 7.1, Temp. 20°C
Han river, DOC: 2.4 mg/l
Suwannee, DOC: 1.5 mg/l
Aldrich, DOC: 1.0 mg/l

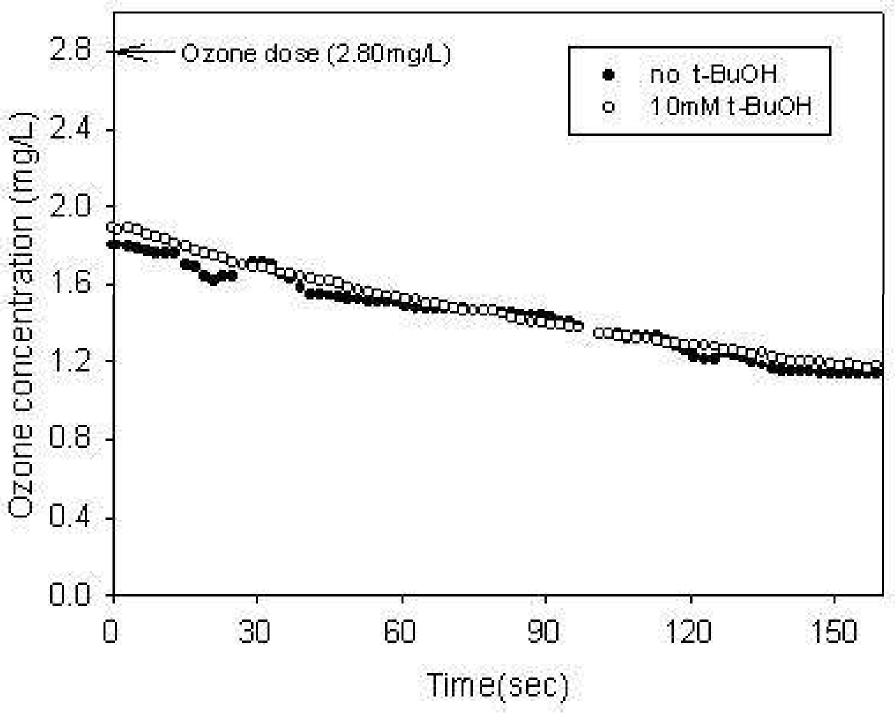
Mechanism of ozone decomposition

- **Ozone decomposition – Role of ozone and OH radical**

1. Suwannee River, USA



2. Han River, Korea



1. Presence of large IOD constitution (30 ~ 50 % of the initial ozone dose)

2. Suwannee River : a large portion of the OH radical mediated reaction for the IOD

3. Han River : the absence of OH radical mediated reaction for the IOD

R_{ct} Concept

$$R_{ct} = \int_0^T [\bullet OH]_t \;/\; \int_0^T [O_3]_t$$

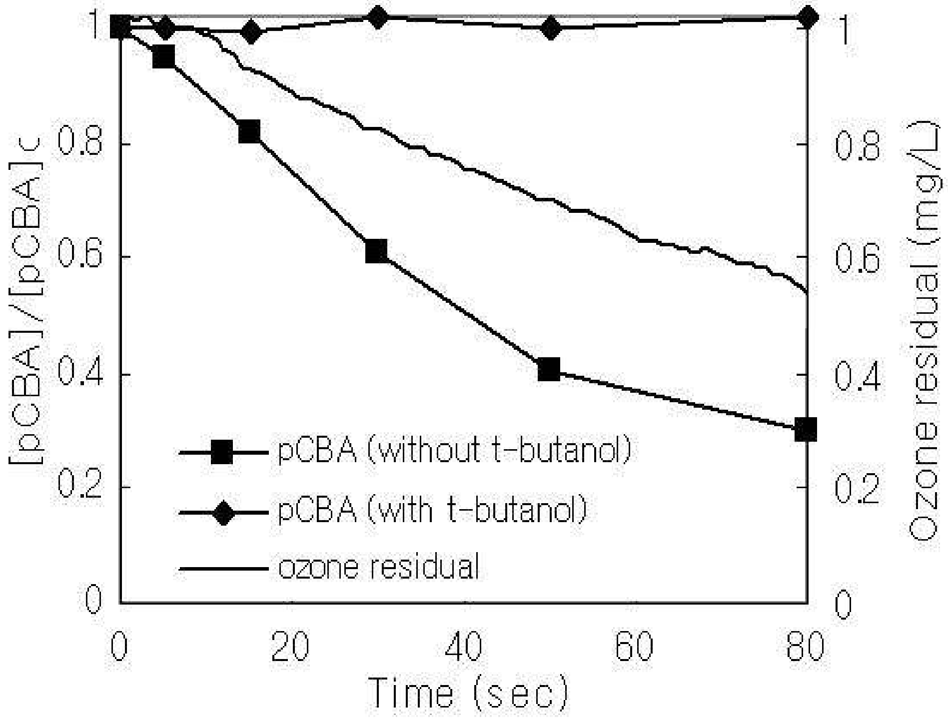
$$\mathrm{Ln}([pCBA]/[pCBA]_0) = -\ k_{OH,,pCBA} \int_0^T [OH]_t\, dt$$

$$= -\ R_{ct}\ k_{OH,,pCBA} \int_0^T [O_3]_t\, dt$$

Elovitz & von Gunten, 1999

Ozone oxidation

- **R_{ct} concept;** the ratio of ozone exposure to that of OH radicals



$$R_{ct} = [\cdot OH]/[O_3]$$

$$\frac{-d[pCBA]}{dt} = k_{\bullet OH,pCBA}[pCBA][\bullet OH]$$

$$\ln\left(\frac{[pCBA]}{[pCBA]_0}\right) = -k_{\bullet OH,pCBA} R_{ct} \int_0^t [O_3]dt$$

$$R_{ct} = \ln\left(\frac{[pCBA]}{[pCBA]_0}\right) \Big/ -k_{\bullet OH,pCBA} \int_0^t [O_3]dt$$

R_{ct} was calculated to 4.25×10^{-7} in Han River water

Quantification of OH radicals would be calculated using the R_{ct} concept, which is defined as the ratio of ozone exposure to that of OH radicals

Role of NOM on ozone disinfection

- **Han River water**

  HS (scavenging) >> HS (promoting)

  $R_{ct} = 4.3 \times 10^{-7}$, (pH 8.2, $[DOC]_0 = 2.4$ mg/l)

- **Aldrich humic acid**

  HS (promoting) >> HS (scavenging)

  $R_{ct} = 5.5 \times 10^{-5}$, (pH 8.2, $[DOC]_0 = 1.5$ mg/l)

- **NOM can contribute to enhancing microbial inactivation by generating more OH radical formation**

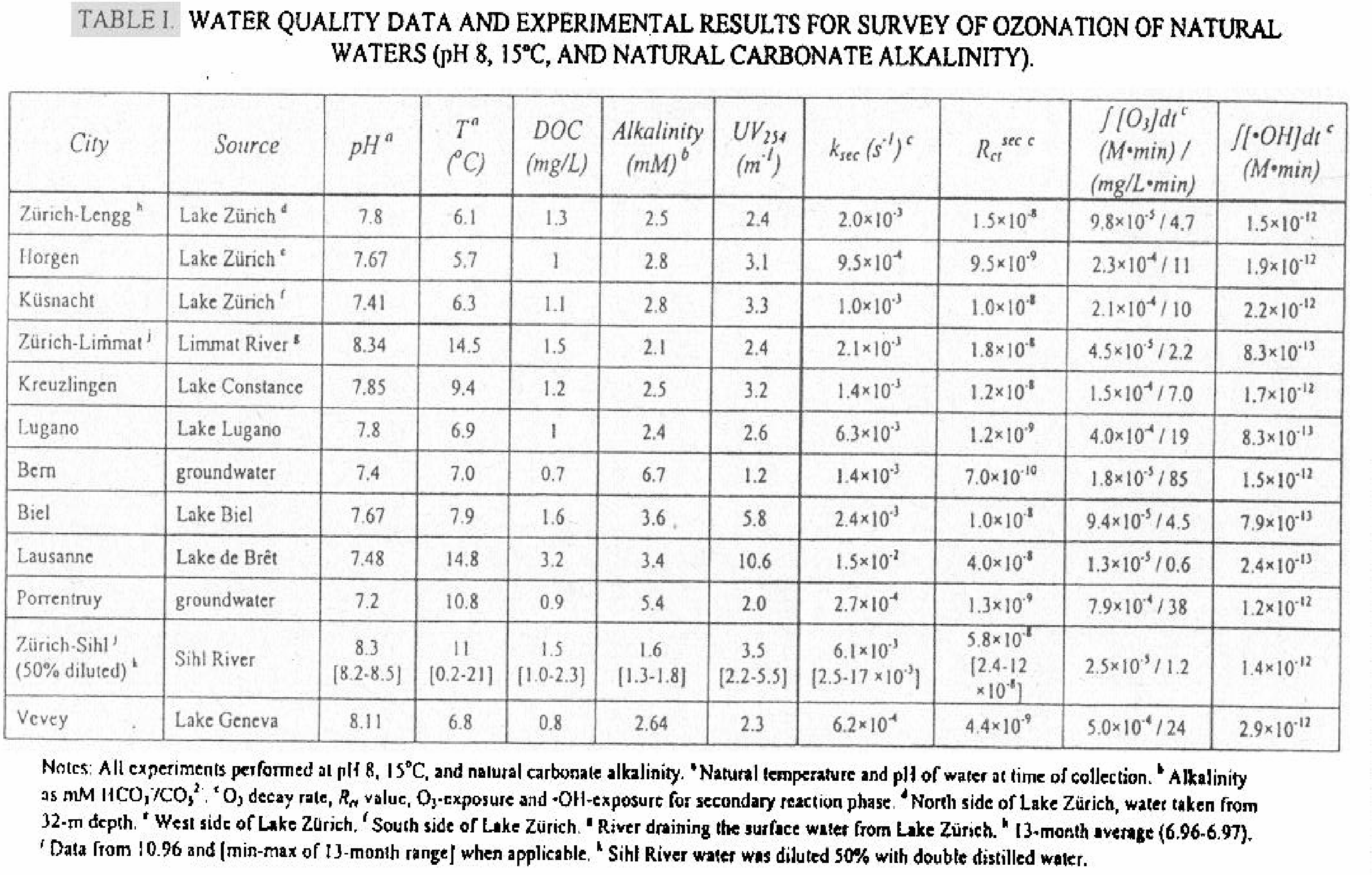


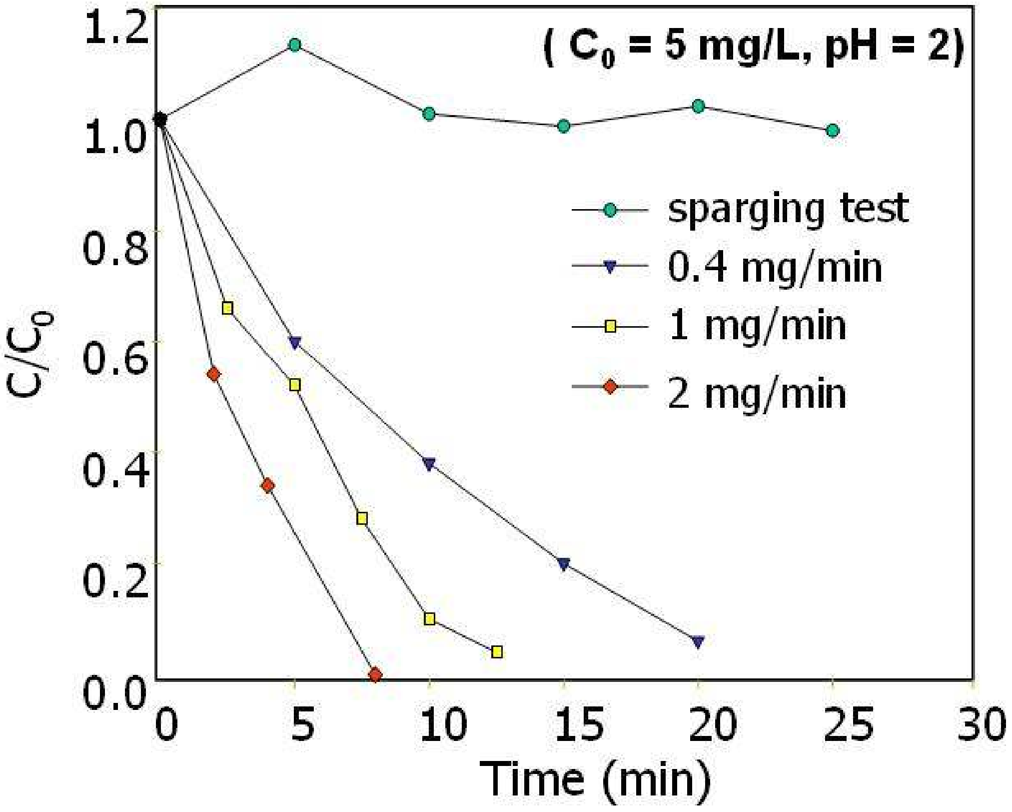
TABLE I. **WATER QUALITY DATA AND EXPERIMENTAL RESULTS FOR SURVEY OF OZONATION OF NATURAL WATERS (pH 8, 15°C, AND NATURAL CARBONATE ALKALINITY).**

City	*Source*	*pH*[a]	T^a (°C)	*DOC* (mg/L)	*Alkalinity* (mM)[b]	UV_{254} (m^{-1})	k_{sec} (s^{-1})[c]	R_{ct}^{sec}[c]	$\int[O_3]dt$[c] (M•min) / (mg/L•min)	$\int[\cdot OH]dt$[c] (M•min)
Zürich-Lengg[h]	Lake Zürich[d]	7.8	6.1	1.3	2.5	2.4	2.0×10^{-3}	1.5×10^{-8}	9.8×10^{-5} / 4.7	1.5×10^{-12}
Horgen	Lake Zürich[e]	7.67	5.7	1	2.8	3.1	9.5×10^{-4}	9.5×10^{-9}	2.3×10^{-4} / 11	1.9×10^{-12}
Küsnacht	Lake Zürich[f]	7.41	6.3	1.1	2.8	3.3	1.0×10^{-3}	1.0×10^{-8}	2.1×10^{-4} / 10	2.2×10^{-12}
Zürich-Limmat[j]	Limmat River[g]	8.34	14.5	1.5	2.1	2.4	2.1×10^{-3}	1.8×10^{-8}	4.5×10^{-5} / 2.2	8.3×10^{-13}
Kreuzlingen	Lake Constance	7.85	9.4	1.2	2.5	3.2	1.4×10^{-3}	1.2×10^{-8}	1.5×10^{-4} / 7.0	1.7×10^{-12}
Lugano	Lake Lugano	7.8	6.9	1	2.4	2.6	6.3×10^{-3}	1.2×10^{-9}	4.0×10^{-4} / 19	8.3×10^{-13}
Bern	groundwater	7.4	7.0	0.7	6.7	1.2	1.4×10^{-3}	7.0×10^{-10}	1.8×10^{-5} / 85	1.5×10^{-12}
Biel	Lake Biel	7.67	7.9	1.6	3.6	5.8	2.4×10^{-3}	1.0×10^{-8}	9.4×10^{-5} / 4.5	7.9×10^{-13}
Lausanne	Lake de Brêt	7.48	14.8	3.2	3.4	10.6	1.5×10^{-2}	4.0×10^{-8}	1.3×10^{-5} / 0.6	2.4×10^{-13}
Porrentruy	groundwater	7.2	10.8	0.9	5.4	2.0	2.7×10^{-4}	1.3×10^{-9}	7.9×10^{-4} / 38	1.2×10^{-12}
Zürich-Sihl[j] (50% diluted)[k]	Sihl River	8.3 [8.2-8.5]	11 [0.2-21]	1.5 [1.0-2.3]	1.6 [1.3-1.8]	3.5 [2.2-5.5]	6.1×10^{-3} [2.5-17×10^{-3}]	5.8×10^{-8} [2.4-12 $\times10^{-8}$]	2.5×10^{-5} / 1.2	1.4×10^{-12}
Vevey	Lake Geneva	8.11	6.8	0.8	2.64	2.3	6.2×10^{-4}	4.4×10^{-9}	5.0×10^{-4} / 24	2.9×10^{-12}

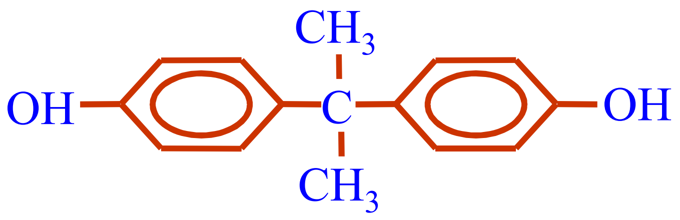
Notes: All experiments performed at pH 8, 15°C, and natural carbonate alkalinity. [a] Natural temperature and pH of water at time of collection. [b] Alkalinity as mM HCO_3^-/CO_3^{2-}. [c] O_3 decay rate, R_{ct} value, O_3-exposure and ·OH-exposure for secondary reaction phase. [d] North side of Lake Zürich, water taken from 32-m depth. [e] West side of Lake Zürich. [f] South side of Lake Zürich. [g] River draining the surface water from Lake Zürich. [h] 13-month average (6.96-6.97). [j] Data from 10.96 and [min-max of 13-month range] when applicable. [k] Sihl River water was diluted 50% with double distilled water.

Ozone oxidation

- **Degradation of Bisphenol A by ozone**



Bisphenol A



Endocrine disruptor

Widely used as a raw material of polycarbonate plastics & epoxy resin

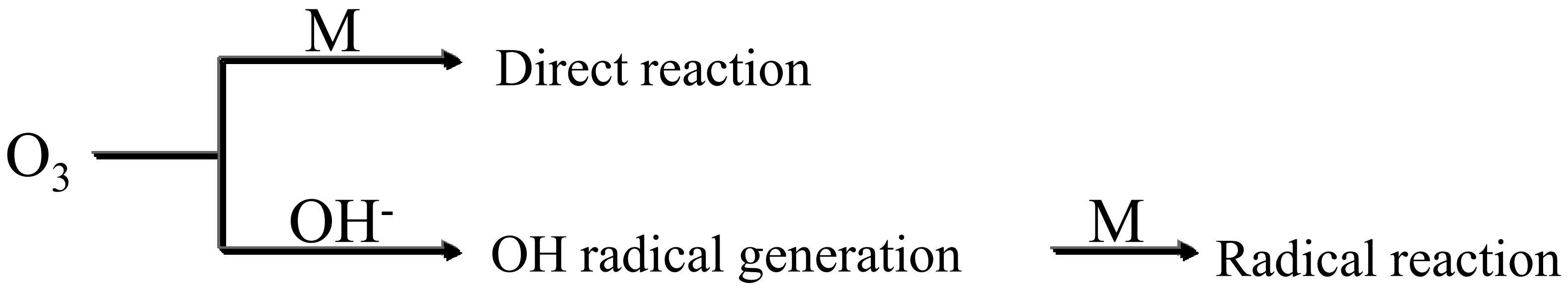
Recently, detected in baby bottles

5mg/L of Bisphenol A was successfully oxidized within 10 min at 2mg/min (0.91mg/Lmin)

Ozone oxidation

- **Degradation of Bisphenol A by ozone and by OH radicals**

Ozone Reaction Characteristics



O_3

M

Direct reaction

OH^-

OH radical generation

M

Radical reaction

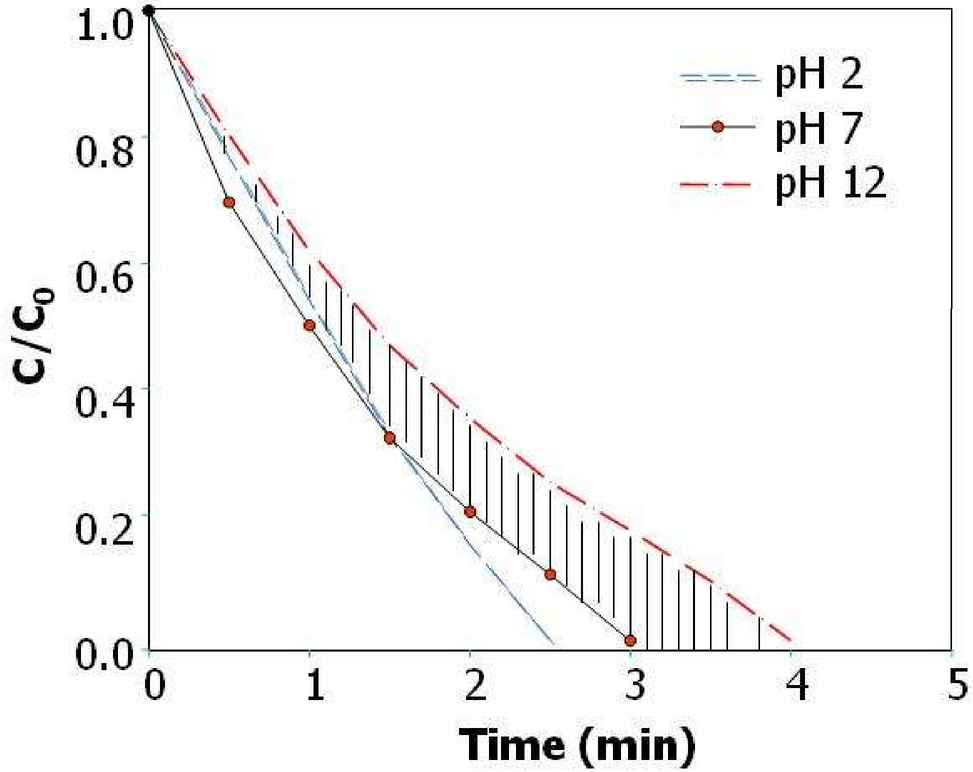
M: Bisphenol A

$$\frac{d[bisphenol\ \ A]}{dt}=-(k_d[O_3]+k_{OH}[\cdot OH])[biophenol\ \ A]$$

Ozone oxidation

- **Effect of pH on Bisphenol A Degradation**

(C_0 = 1 mg/L, F_{O3} = 1 mg/L, 10 mg/L t-BuOH)



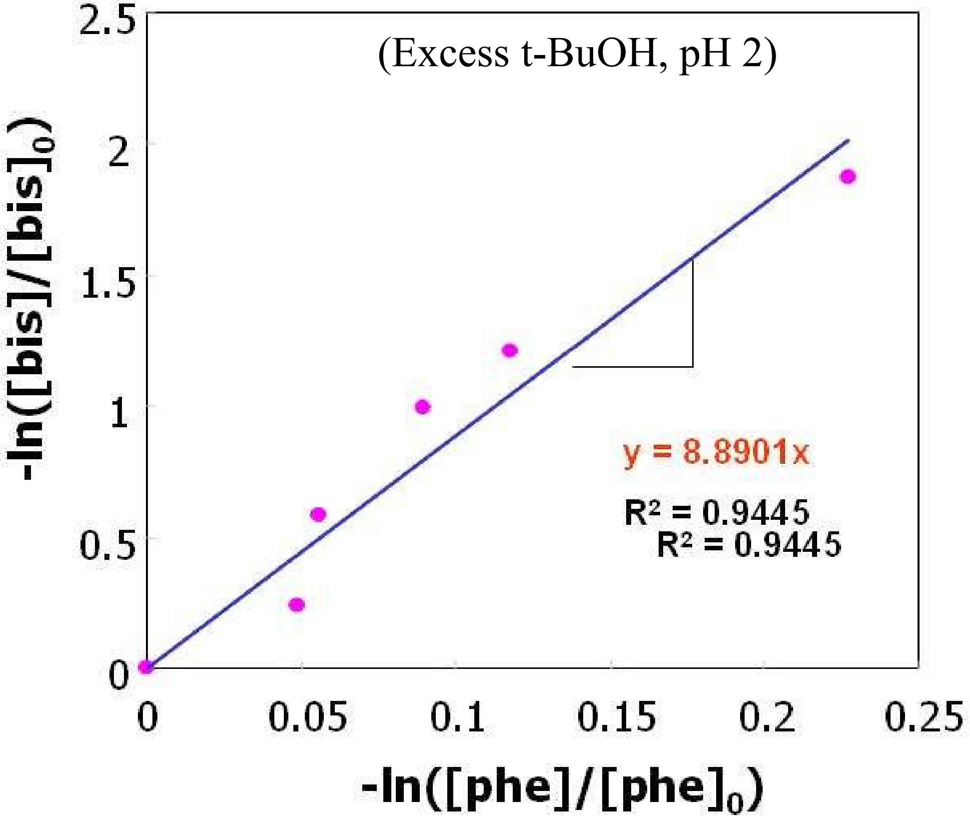
OH radical generation

At pH 12, the O_3 initiated radical reaction exists (shadowed area, 10-20%)

At pH 7, the O_3 initiated radical reaction is negligible.

Ozone oxidation

- **Comparative kinetic study for ozone rate constant**



(Excess t-BuOH, pH 2)

$$bisphenol\ A + O_3 \xrightarrow{k_{bis}} products$$

$$phenol + O_3 \xrightarrow{k_{phe}} products$$

$$\ln\left(\frac{[bisphenol\ A]_t}{[bisphenol\ A]_0}\right) = \frac{k_{bis}}{k_{phe}} \ln\left(\frac{[phenol]_t}{[phenol]_0}\right)$$

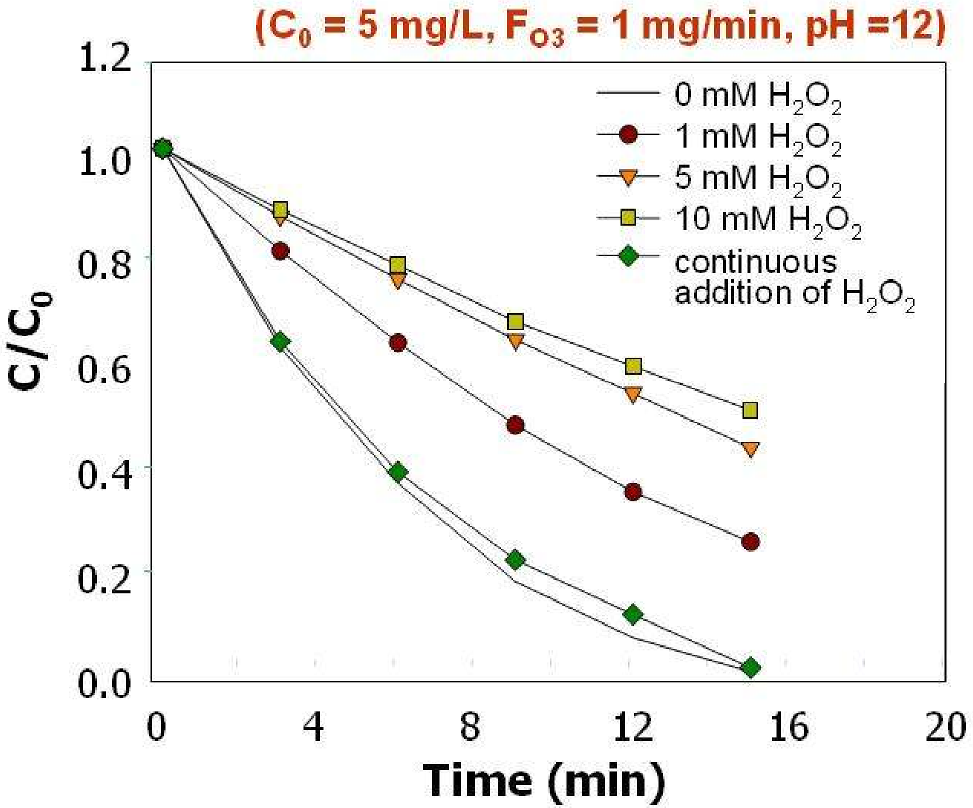
K_{phe} : literature values are available

$$slope = \frac{k_{bis}}{k_{phe}}$$

$K_{phe} = 1.5 \times 10^3\ M^{-1}\ s^{-1}$ ⇨ $K_{bis} = 1.3 \times 10^4\ M^{-1}\ s^{-1}$

Ozone oxidation

- **Effect of H_2O_2 on Bisphenol A Degradation**

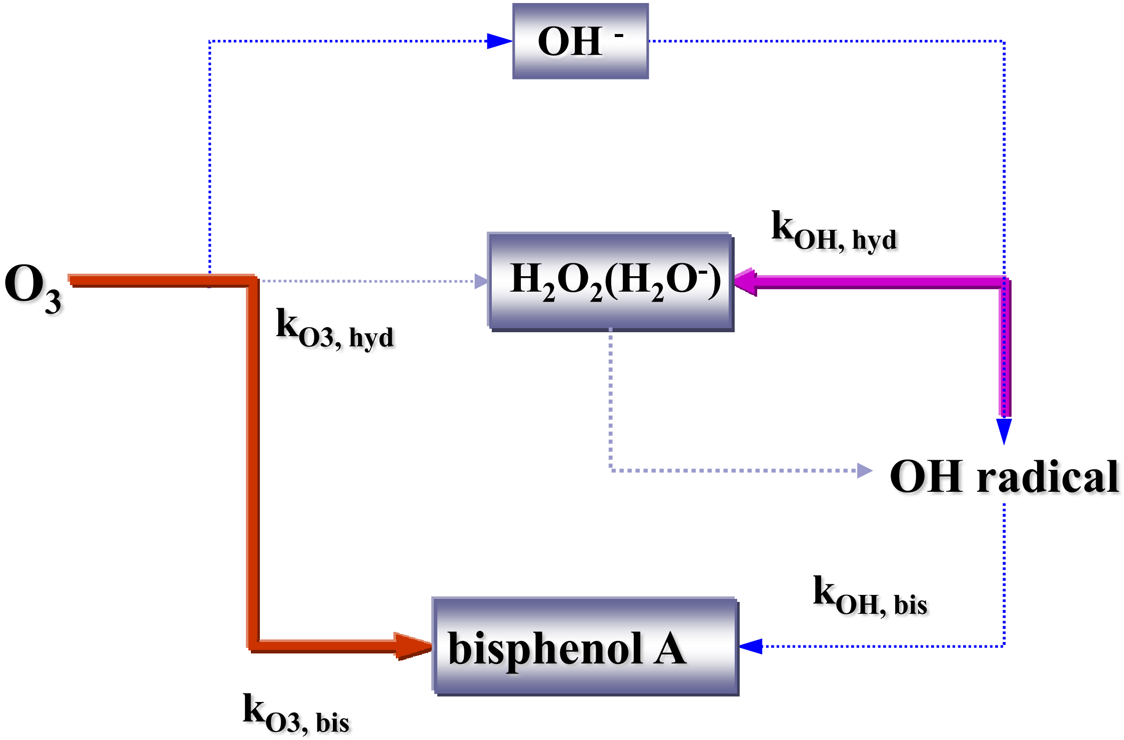


In spite of the enhanced generation of OH radical with H_2O_2 addition, the degradation of bisphenol A did not increased

⇨ The direct reaction dominates the reaction pathway of bisphenol A degradation

Ozone oxidation

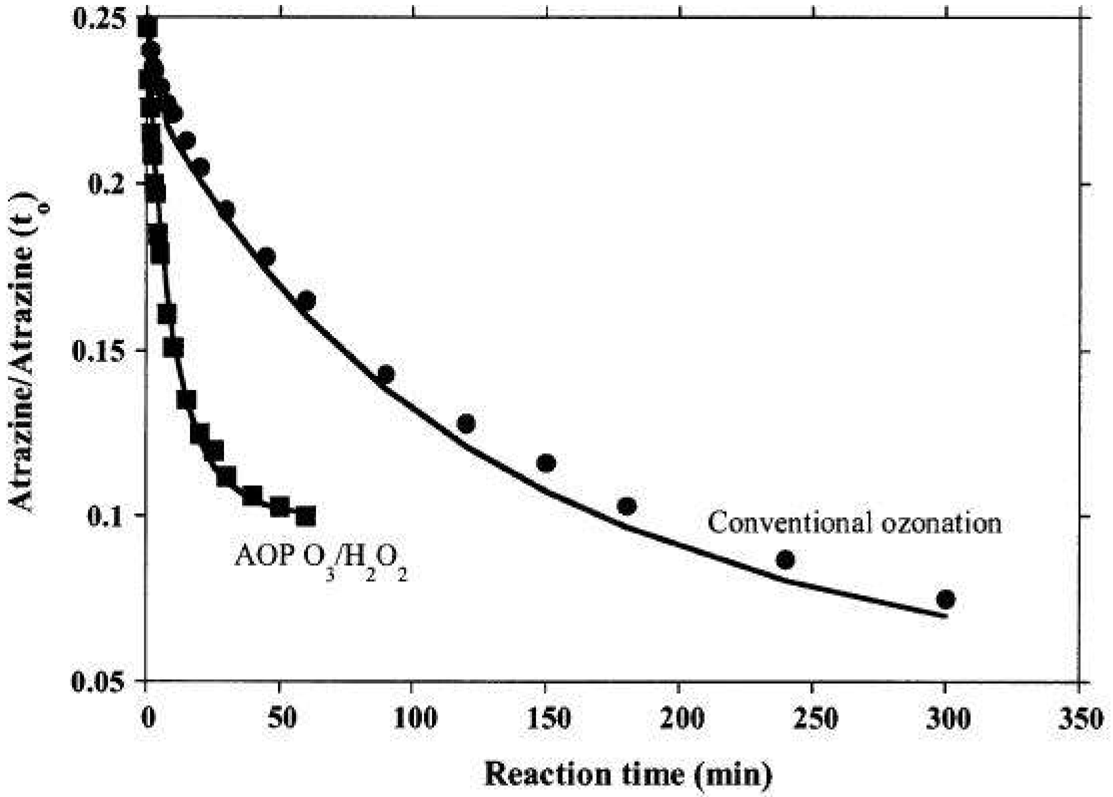
- **Effect of H_2O_2 on Bisphenol A Degradation**



The direct reaction dominates the reaction pathway of bisphenol A degradation

Ozone oxidation

- **Oxidation of atrazine during O_3 and O_3/H_2O_2**



Addition of H_2O_2 : enhance the production of OH radical

Symbol : measured result; line : calculated using R_c value and ozone residual

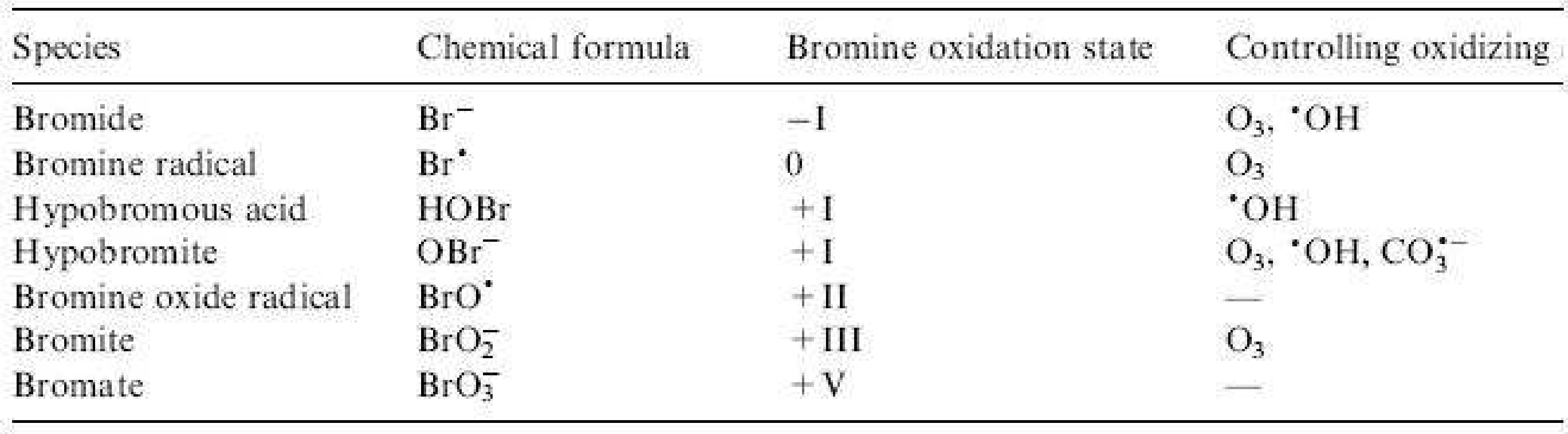
The good agreement between measured and calculated data confirm the R_c concept

Ozonation by—products

- **Bromine species formed during bromate formation**

Bromate is formed in ozonation processes from the oxidation of bormide through a Combination of ozone and OH radical reactions.

Its formation includes up to six oxidation states of bromine



Species	Chemical formula	Bromine oxidation state	Controlling oxidizing
Bromide	Br^-	−I	O_3, $^\bullet OH$
Bromine radical	$Br^\bullet$	0	O_3
Hypobromous acid	$HOBr$	+I	$^\bullet OH$
Hypobromite	OBr^-	+I	O_3, $^\bullet OH$, $CO_3^{\bullet -}$
Bromine oxide radical	$BrO^\bullet$	+II	—
Bromite	BrO_2^-	+III	O_3
Bromate	BrO_3^-	+V	—

Because both oxidants can act simultaneously or in sequence on various oxidation levels, the whole reaction system is extremely complicated and highly non-linear.

Ozonation by–products

- **Bromine species formed during bromate formation**

Bromate

$Br^- + O_3 \rightarrow OBr^-$ $(HOBr \leftrightarrow H^+ + OBr^-)$

$OBr^- + O_3 \rightarrow BrO_3^-$

Molecular Ozone Pathway

$OBr^- + O_3 \rightarrow BrO_3^-$

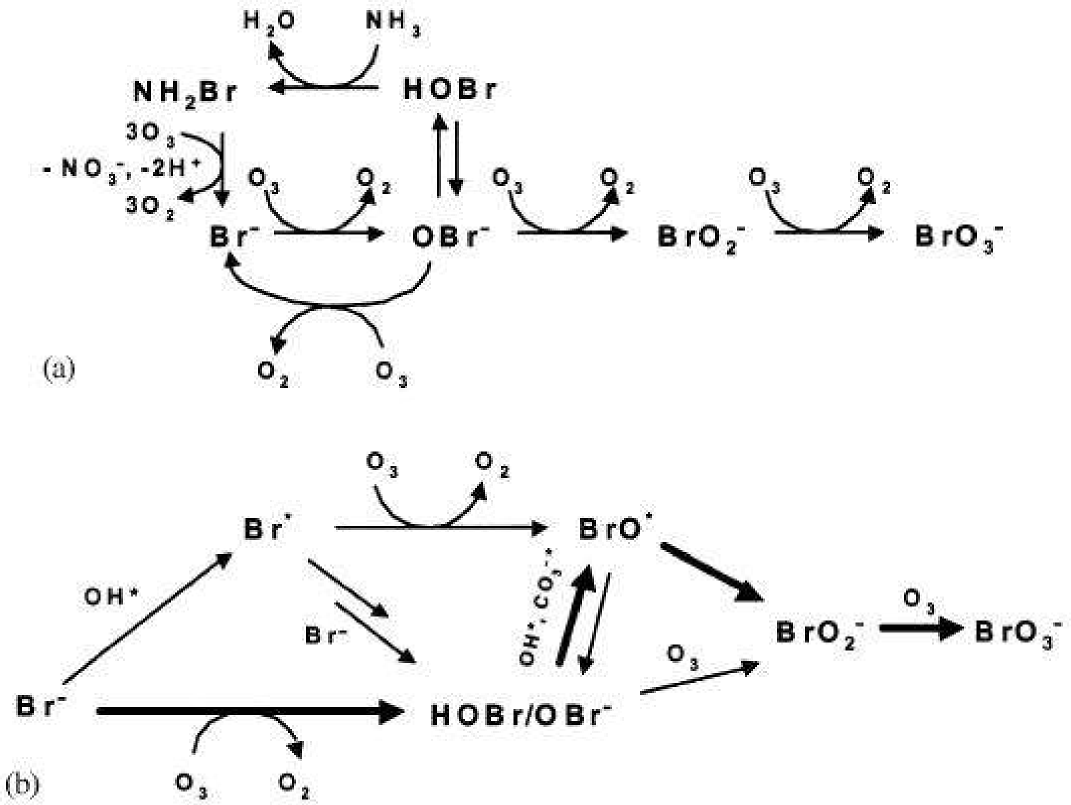
OH Radicals Pathway

$Br^- + \cdot OH \rightarrow BrO_3^-$

1. OH radical reaction is dominant pathway in the presence of NOM
2. Br^- Conversion to BrO_3^-: 0 – 50 % (ICR: < 10 %, on average)

Ozonation by−products

- **Reaction scheme for bromate formation**



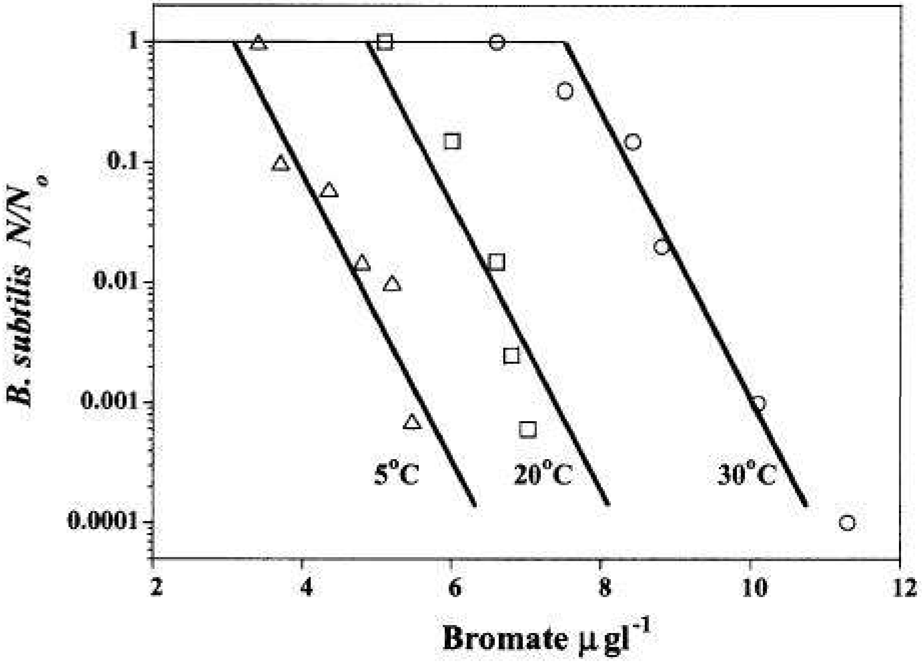
(a) Reaction with ozone

(b) Reaction with ozone and OH radicals

The bold lines show the main pathway during the secondary phase of an ozonation process

Ozonation by—products

- **Inactivation of *B. subtilis* spores and bromate formation**

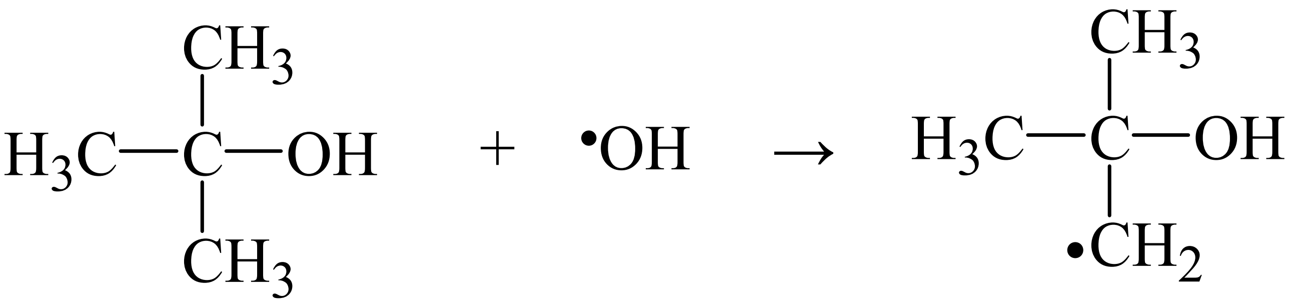


The occurrence of more resistant pathogens such as *C. parvum* oocysts leads to a demand for increased CT. Therefore, in waters with bromide levels above 50 ug/l, bromate formation may exceed the drinking water standard

One of the decisive factors is the temperature of the treated water. Both the efficiency of inactivation of microorganisms and bromate formation increase with increasing temperature

t−BuOH, an effective •OH scavenger ?

- To be an effective •OH scavenger ➔ No effect of reaction product with •OH on the system



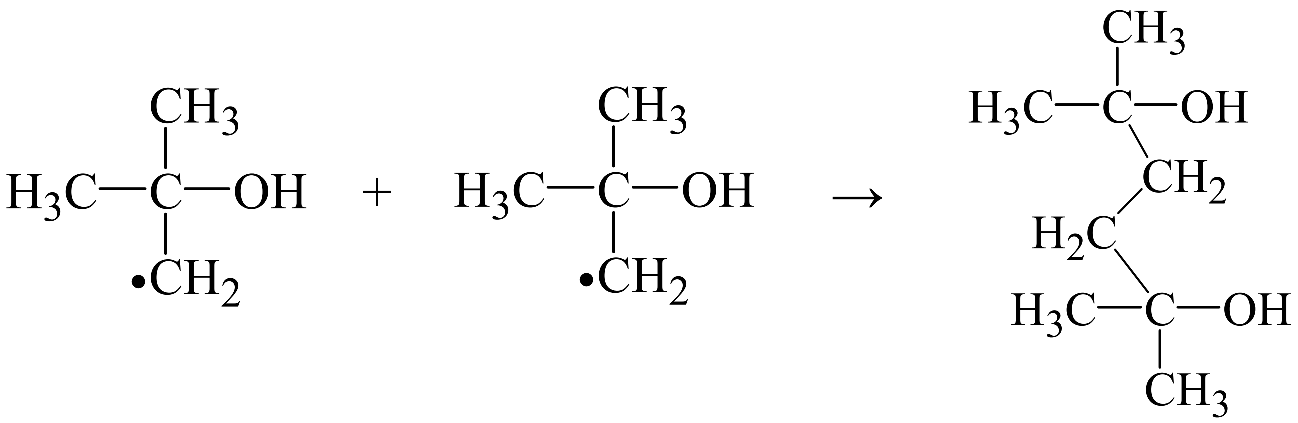
$$H_3C-C(CH_3)_2-OH + {}^{\bullet}OH \rightarrow H_3C-C(CH_3)({}^{\bullet}CH_2)-OH$$

t-BuOH

β-hydroxyalkyl radical (R•)

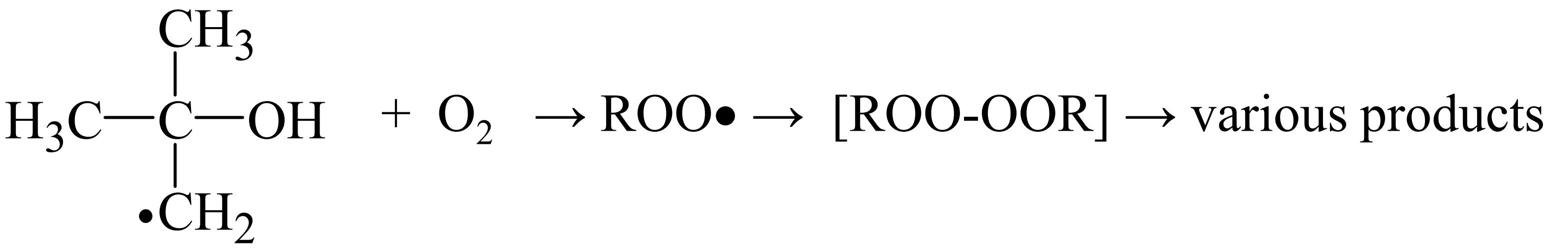
Why is t−BuOH commonly used as •OH scavenger ?

- In the absence of oxygen ➔ stabilized through dimerization



$$H_3C-\overset{CH_3}{\underset{\bullet CH_2}{C}}-OH + H_3C-\overset{CH_3}{\underset{\bullet CH_2}{C}}-OH \rightarrow H_3C-\overset{CH_3}{C}(OH)-CH_2-CH_2-\underset{CH_3}{C}(OH)-CH_3$$

- In the presence of oxygen ➔ peroxyradical (ROO•) 형성후 다양한 화합물 생성



$$H_3C-\overset{CH_3}{\underset{\bullet CH_2}{C}}-OH + O_2 \rightarrow ROO\bullet \rightarrow [ROO\text{-}OOR] \rightarrow \text{various products}$$

(다른 RO_2와는 달리 자체 분해를 통해 HO_2 라디칼을 생성하지 않는다.)

반도체 공정에서 AOP 응용

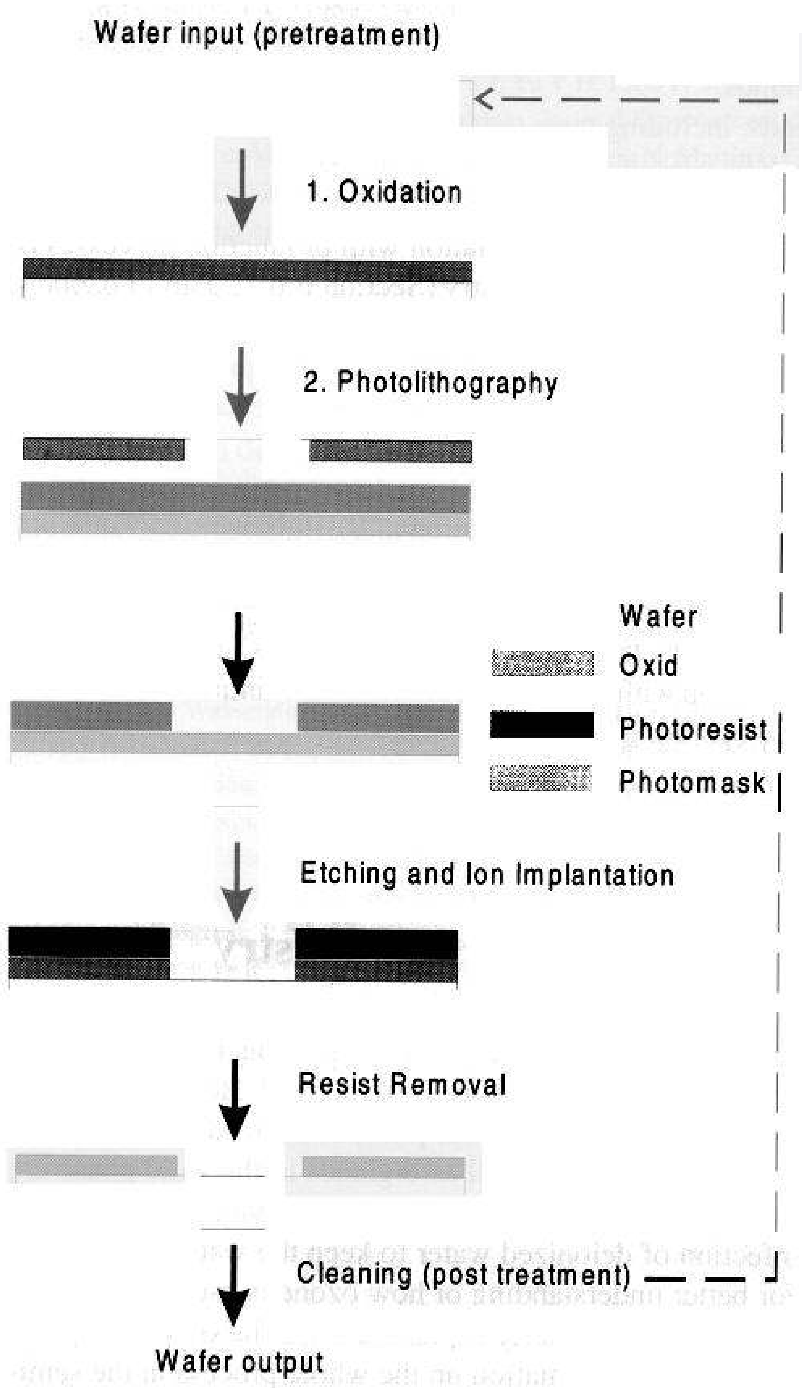


Figure 6-1: Process sequence (simplified).

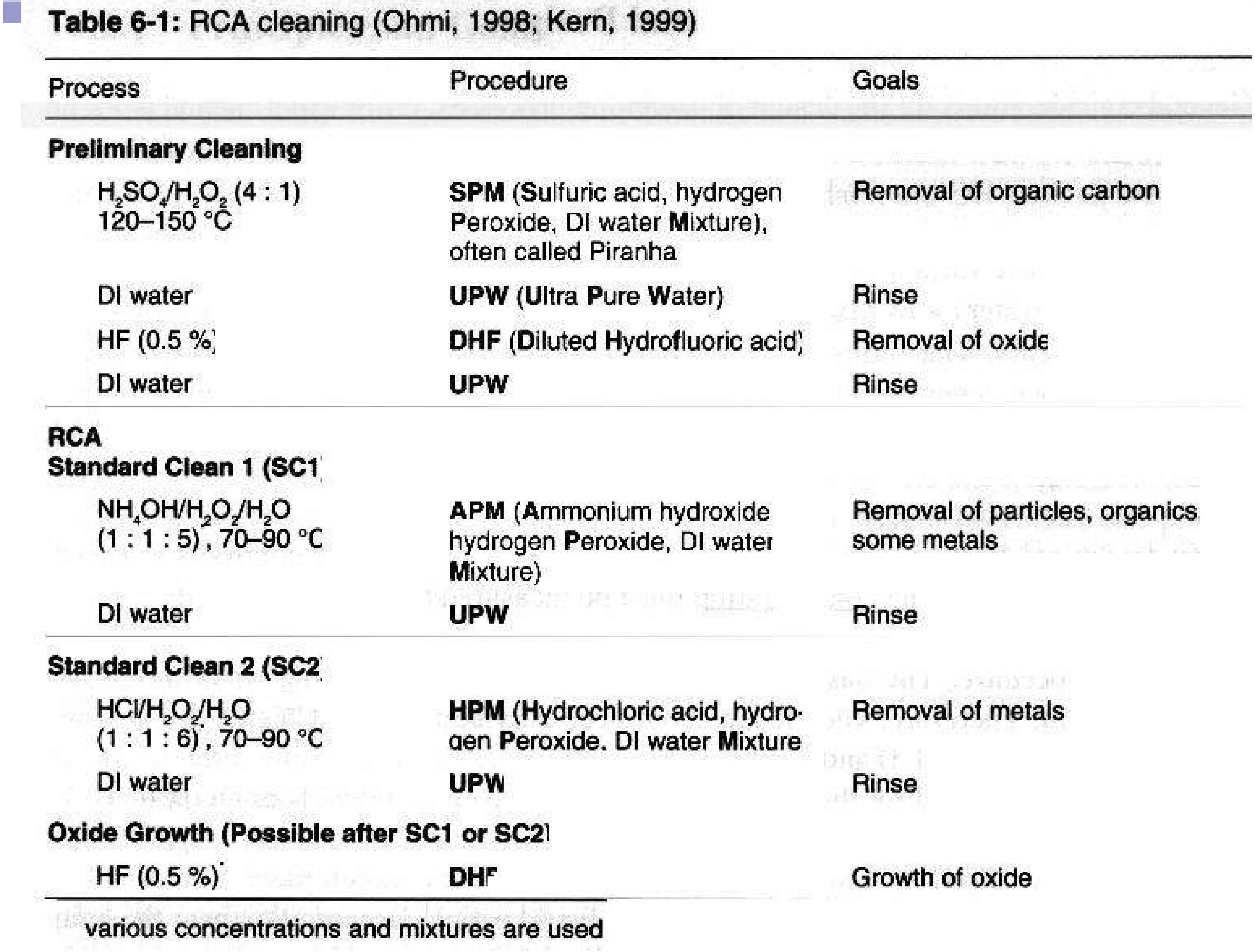
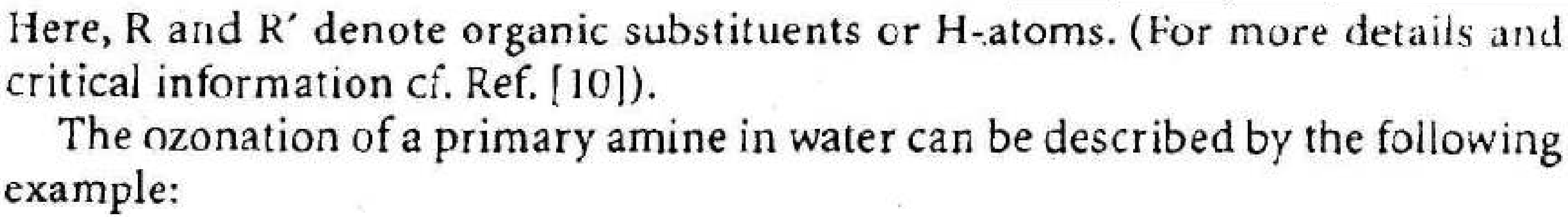


Table 6-1: RCA cleaning (Ohmi, 1998; Kern, 1999)

Process	Procedure	Goals
Preliminary Cleaning		
H_2SO_4/H_2O_2 (4 : 1) 120–150 °C	**SPM** (**S**ulfuric acid, hydrogen **P**eroxide, DI water **M**ixture), often called Piranha	Removal of organic carbon
DI water	**UPW** (**U**ltra **P**ure **W**ater)	Rinse
HF (0.5 %)	**DHF** (**D**iluted **H**ydro**f**luoric acid)	Removal of oxide
DI water	**UPW**	Rinse
RCA **Standard Clean 1 (SC1)**		
$NH_4OH/H_2O_2/H_2O$ (1 : 1 : 5)*, 70–90 °C	**APM** (**A**mmonium hydroxide hydrogen **P**eroxide, DI water **M**ixture)	Removal of particles, organics some metals
DI water	**UPW**	Rinse
Standard Clean 2 (SC2)		
$HCl/H_2O_2/H_2O$ (1 : 1 : 6)*, 70–90 °C	**HPM** (**H**ydrochloric acid, hydrogen **P**eroxide, DI water **M**ixture	Removal of metals
DI water	**UPW**	Rinse
Oxide Growth (Possible after SC1 or SC2)		
HF (0.5 %)*	**DHF**	Growth of oxide

* various concentrations and mixtures are used



- Here, R and R′ denote organic substituents or H-atoms. (For more details and critical information cf. Ref. [10]).

The ozonation of a primary amine in water can be described by the following example:

2.2

Rate Law for Molecular Ozone Reactions

$$O_3 + M \xrightarrow{k_M} M_{oxid} \qquad (9)$$

$$-d[M]_t/dt = \boxed{k_M} \cdot [M]_t^1 \cdot [O_3]_t^1 = \boxed{\eta\, k_{O_3}} \cdot [M]_t^1 \cdot [O_3]_t^1 \qquad (10)$$

$$\int([O_3](t) \cdot dt) \rightarrow [\overline{O_3}] \cdot t = c \cdot t \qquad (13)$$

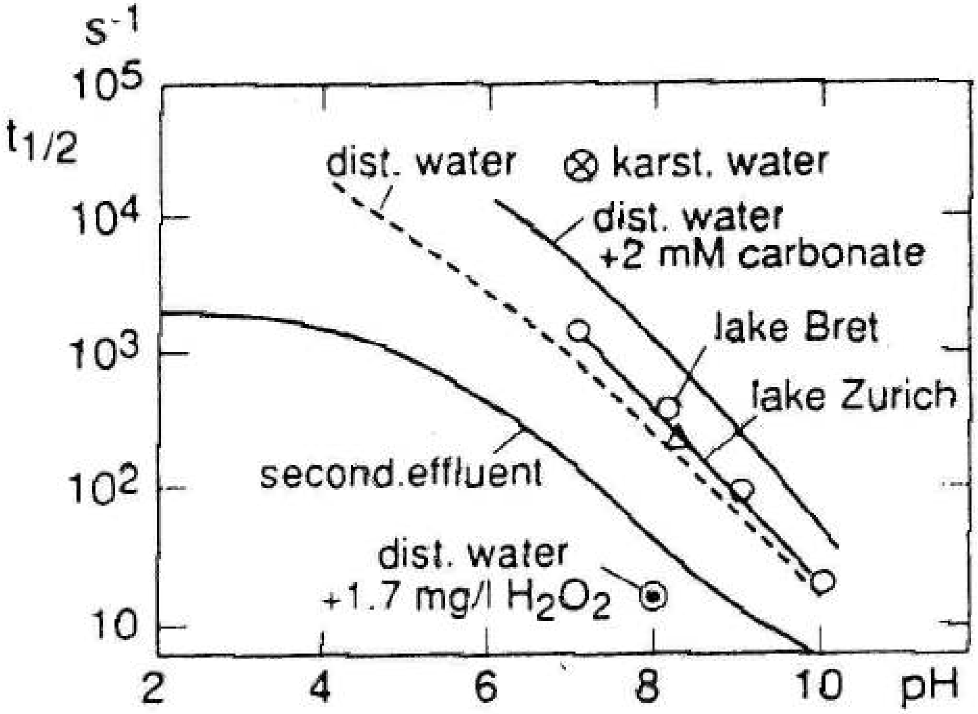


Fig. 7. Second half-life of ozone ($t_{1/2}$) dosed to different types of water as a function of pH. Within this time the concentration of ozone (about 3 mg/l at beginning of measurement) declined from 50% to 25%. For details of measurement cf. [45, 46].

- distilled water: pH adjusted with phosphate buffer (0.05 M)
- karstic groundwater: DOC =1.2 mg/l, pH adjusted by NaOH and HCl
- Lake Zurich water: DOC = 1.2 mg/l; diluted to 70%, pH adjusted by NaOH and HCl
- Lac de Bret water: DOC = 3.2 mg/l; diluted to 70%, pH adjusted by NaOH and HCl
- secondary effluent of communal wastewater plant: DOC 7 mg/l, pH adjusted by borate buffer

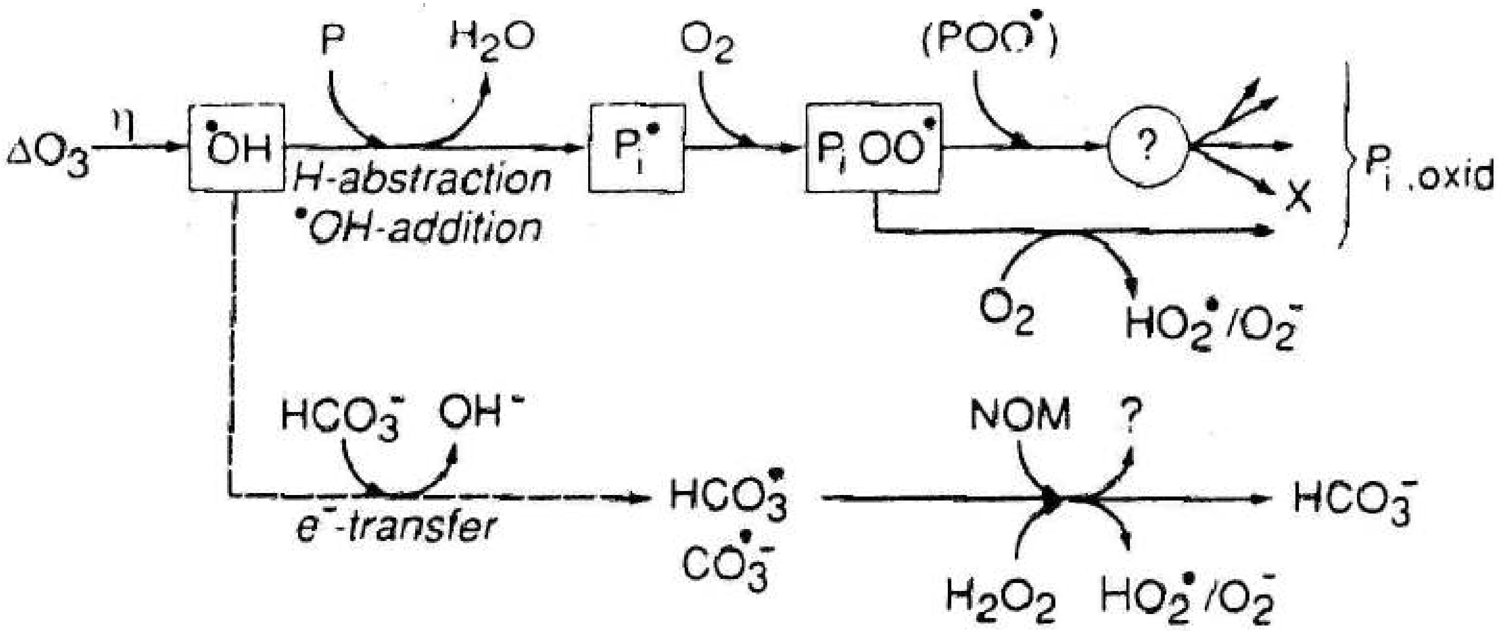


Fig. 10. Reactions of $OH^{\cdot}$ with an organic micropollutant P leading to a great diversity of oxidized compounds. Adapted from [53]

5.2

Rate-Law and Rate-Constants for OH Radical Reactions

$$OH^{\bullet} + M \xrightarrow{k_M} M_{oxid} \tag{17}$$

$$-d\,[M]_t/dt = k_{OH^{\bullet},M}\,[M]_t^1\,[OH^{\bullet}]_t^1 \tag{18}$$

$$-\ln\,[M]_t/[M]_O = k_M \cdot [OH^{\bullet}]_{ss} \cdot t \tag{19}$$

or:

$$[M]_t/[M]_O = e^{-(k_M \cdot [OH^{\bullet}]_{ss} \cdot t)} \tag{20}$$

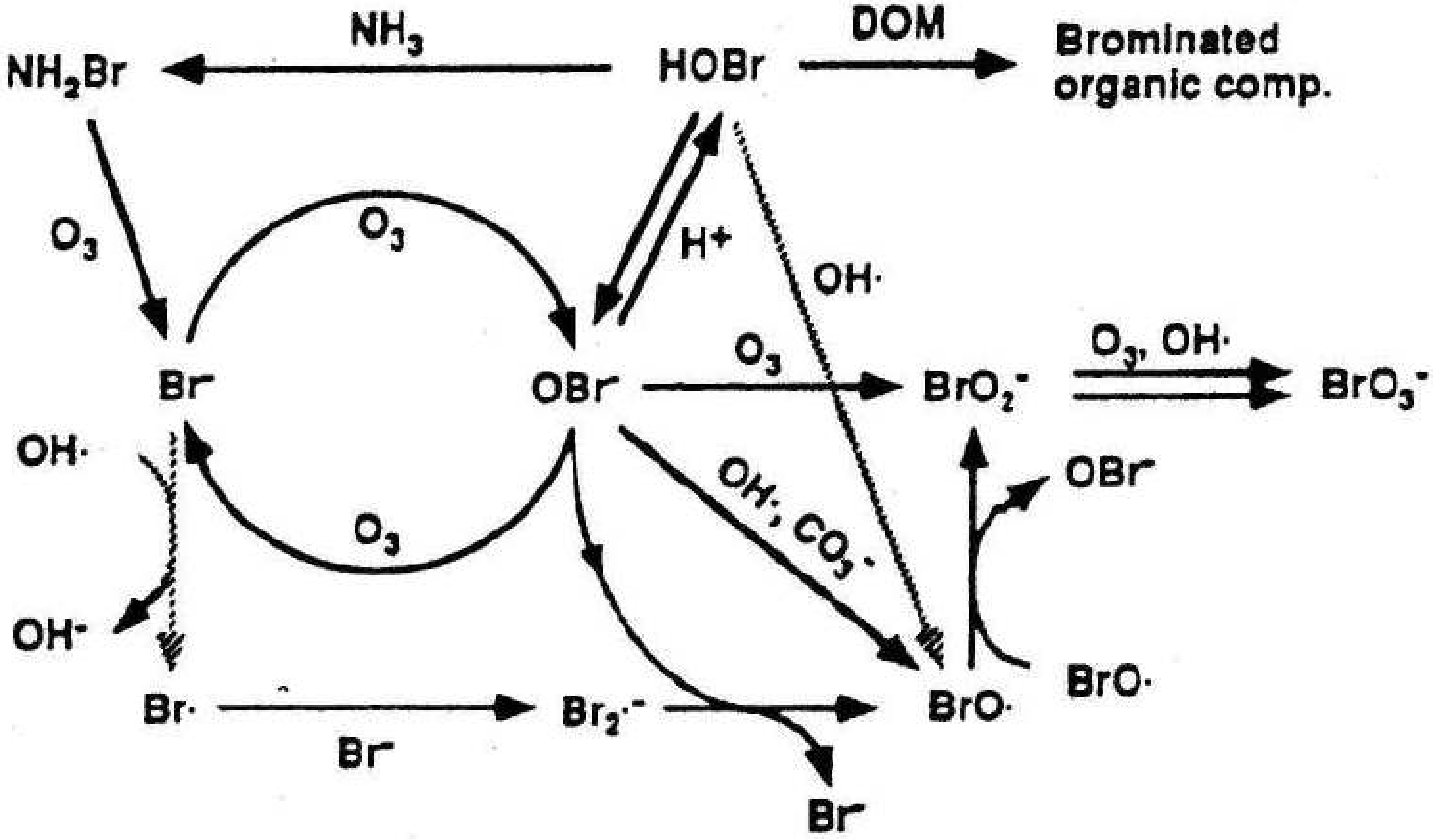


Fig. 19. Reactions upon ozonation of bromide-containing freshwater. Reactions for molecular O_3 (*solid lines*) and $OH^\cdot$ and $HCO_3^\cdot$ radicals (*dashed lines*) are shown [93]

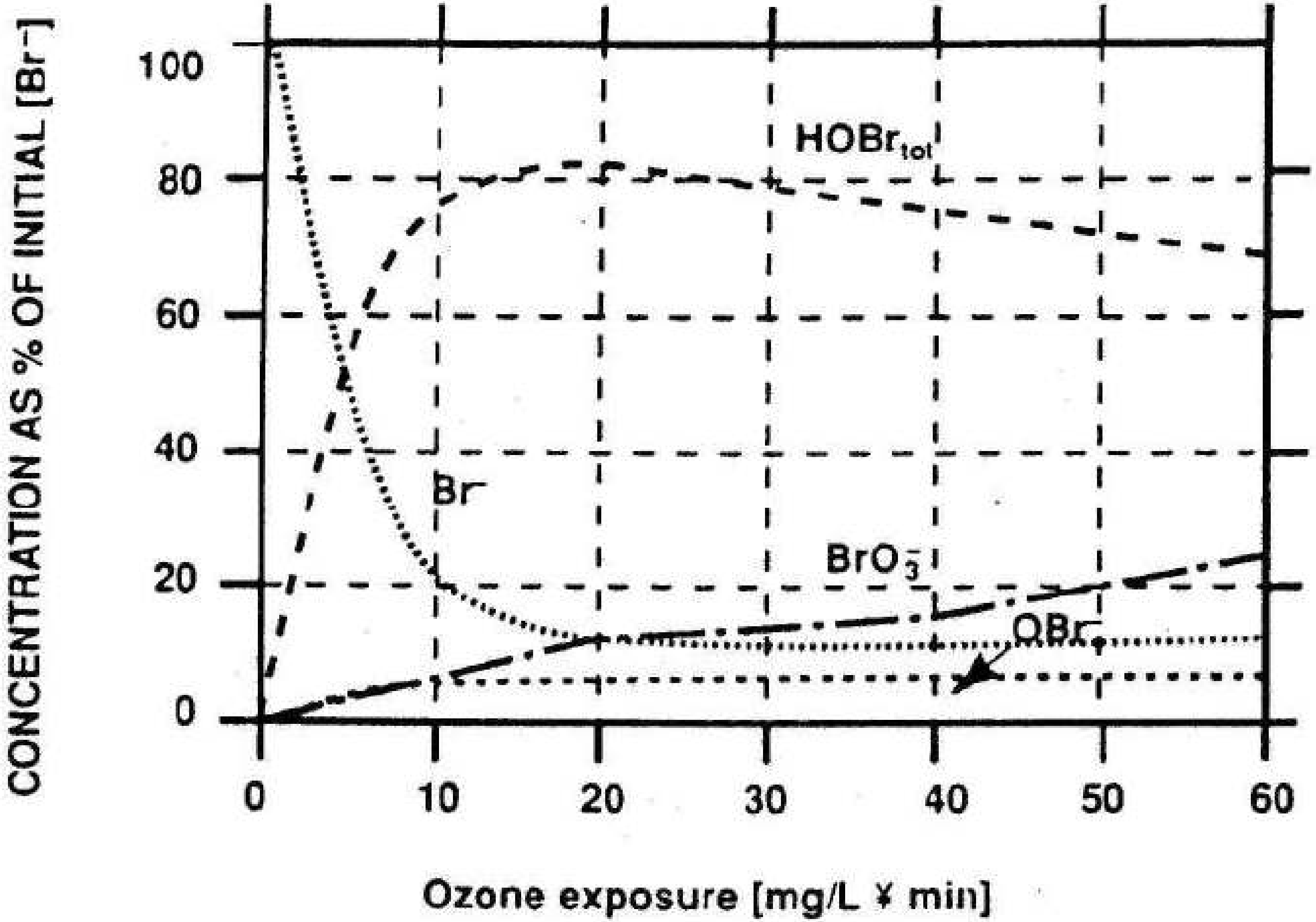


Fig. 20. Model calculations based on 9 reactions for an extended ozonation of a bromide containing water at pH 7 that contains $OH^{\bullet}$-scavengers (absence of $OH^{\bullet}$ mediated reactions). Concentrations of different species are given in percent of initial $[Br^-]$ [62]