DECOMPOSITION RATE OF OZONE IN WATER WITH ULTRAVIOLET RADIATION

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The combination of ozone and UV radiation is useful in removing refractory compounds dissolved in water. In this paper, the decomposition of ozone with UV radiation was investigated by using a rectangular flow reactor equipped with transparent quartz walls. The decomposition rate of ozone in water was proportional to the UV irradiance and the ozone concentration. The dependence on OH^- ion concentration was very weak compared to decomposition without UV radiation. Data were correlated with an experimental equation which was applicable in the pH range of 2–9.

A simulation of ozone utilization in a model reactor indicates that unnecessarily intensive UV radiation destroys ozone in the gas phase before it is transferred into the liquid phase. This loss decreases the amount of ozone decomposed in the liquid phase and hence hinders the ozonation of dissolved pollutants. Ozone absorption and UV radiation have to be carried out in different parts of the reactor.

Introduction

Ozone is one of the strongest oxidizing agents and easily destroys olefins, heterocyclics and nucleophiles. Oxidized products are less harmful than those of chlorination. Therefore, ozonation is attracting much attention as an advanced water treatment process.^{3,6)} However, refractory compounds such as saturated alcohols and carboxylic acids are built up in the system after a certain extent of ozonation, and no further decrease in TOC or COD can be expected. To overcome this problem, combination with UV radiation is useful.⁸⁾ A low-pressure mercury lamp radiates photons mainly at 253.7 nm, providing enough energy to produce free radicals which are much stronger oxidants than ozone itself.

The destruction rate of refractory compounds is closely related to the decomposition rate of ozone. Hoigné and coworkers^{2,9,10)} have investigated rate processes of ozone decomposition in water without UV radiation. When the presence of organic solutes is negligible, the decomposition of ozone involves a chain mechanism initiated by the following reactions.

The propagation is

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Hydrogen peroxide produced in Reaction (5) also enters the chain reaction when its concentration becomes larger than $10^{-4} \text{ mol} \cdot \text{m}^{-3}$.

The chain is suppressed by $\text{HO}_2 \cdot$, which is very unreactive toward ozone. Substances such as formic acid promote the radical chain by producing $\text{O}_2^{\cdot -}$. Bicarbonate and carbonate ions, *t*-butanol etc. scavenge $\text{HO} \cdot$ to form secondary radicals and terminate the chain reaction.

Morooka *et al.*⁵⁾ correlated the decomposition rate of ozone without organic solutes and obtained the following equation.

$$-d[\text{O}_3]/dt = k_a[\text{OH}^-]^{0.28}[\text{O}_3]^{1.5} + k_b[\text{OH}^-][\text{O}_3] \quad (8)$$

$$k_a = 2.1 \times 10^{11} \exp(-74.9 \text{ kJ} \cdot \text{mol}^{-1}/RT) \quad (8a)$$

$$k_b = 1.8 \times 10^{15} \exp(-86.2 \text{ kJ} \cdot \text{mol}^{-1}/RT) \quad (8b)$$

where the unit of concentration is $\text{mol} \cdot \text{m}^{-3}$. The first and second terms on the right-hand side of Eq. (8) are dominant in the range of $\text{pH} < 6$ and $\text{pH} > 8$, respectively. Equation (8) is in good agreement with the literature data though the decomposition rate in the acidic region is not so reproducible and is sensitive to experimental conditions.¹¹⁾

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Ozone in the ambient gas phase is much more stable than in the liquid phase. With the radiation of ultraviolet light, however, ozone decomposes as follows:⁷⁾

This reaction is followed by several reactions which bring further decomposition of ozone. The overall quantum yield for the decomposition of pure ozone is larger than 4.0.⁴⁾ When ozone is diluted with oxygen, transient intermediates such as $\text{O}({}^1\text{D})$ immediately react with oxygen and reproduce ozone. The overall quantum yield tends to zero in this case. In the presence of water vapor, however, hydroxyl radicals are produced by Reaction (10) and take part in the chain reaction.⁷⁾

No practical rate equations for the photolytic decomposition of ozone are available to date.

In this study, the decomposition rate of ozone in water is investigated in the presence of ultraviolet radiation over a wide range of experimental conditions. Further, ozone utilization in a photolytic ozonation reactor is discussed as a function of the UV intensity.

1. Experimental

1.1 Experimental apparatus and flow sheet

Figure 1 shows a schematic diagram of the experimental apparatus. A mixture of ozone and oxygen was bubbled into the bubble column 4 cm in dia. and 25 cm high. The ozone-saturated solution was continuously pumped to the reactor. The concentration of ozone in the liquid stream was measured by iodometry and also by a spectrophotometer equipped with a flow cell. The liquid flow to the reactor or to the spectrophotometer was changed by switching a three-way valve.

Deionized and distilled water was used in the experiment. The pH value of the solution was controlled by injecting aqueous NaOH and H_3PO_4 solutions automatically. The liquid temperature in the absorption column and the reactor was kept at a constant value with the aid of a water-circulating jacket.

Figure 2 shows details of the reactor sectioned by the vertical plane perpendicular to the liquid flow. The reactor was 10 mm wide, 4 mm thick and 190 mm long, and was sandwiched with transparent quartz plates 3 mm thick.

1.2 Measurement of UV irradiance

A low-pressure mercury lamp (20W, 30 cm long) was a source of UV radiation. The lamp emits principally at 253.7 nm, and the UV intensity (UV irradiance) in the reactor was varied by changing the

Fig. 1. Schematic diagram of experimental apparatus.

Fig. 2. Details of reactor sectioned by vertical plane perpendicular to liquid flow.

distance between the lamp and the reactor. The UV irradiance was measured by potassium ferrioxalate ($\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$) actinometry. The concentration of reduced Fe^{2+} ions was determined by spectrophotometry at 510 nm after coloration with 1,10-phenanthroline.

Initially, the reactor was emptied and the UV irradiance at the upper plane of the lower quartz plate (the lower surface of the reactor), I_1 , was measured as a function of lamp distance. The UV irradiance at the lower plane of the upper quartz plate (the upper surface of the reactor), I_0 , was then calculated by correcting the reactor thickness. The value of I_1 was not affected by an ozone-free solution in the reactor. When a solution containing ozone flowed through the reactor, however, the irradiance and the ozone concentration differed locally. In this case, I_1 was determined as an average value along the flow direction and was related to the average ozone concentration as follows:

$$-\log(I_1/I_0) = a_L l [\text{O}_3]_{lm} \quad (11)$$

where $a_L = 360 \text{ mol}^{-1} \cdot \text{m}^2$ for 253.7 nm , and $l = 4 \times 10^{-3} \text{ m}$. $[\text{O}_3]_{lm}$ is the logarithmic mean of the inlet and outlet concentrations of ozone. **Figure 3** indicates that Eq. (11) is valid under the tested conditions. The UV irradiance averaged over the whole reactor was finally calculated from

$$\bar{I} = (I_1 - I_0) / \ln(I_1/I_0) \quad (12)$$

The experiment was carried out at $279\text{--}303 \text{ K}$ and $\text{pH } 2\text{--}9$. The dissolved ozone concentration was $0.02\text{--}0.35 \text{ mol} \cdot \text{m}^{-3}$, and the mean UV irradiance was $2\text{--}40 \text{ W} \cdot \text{m}^{-2}$.

2. Results and Discussion

2.1 Decomposition rate of dissolved ozone

Figure 4 shows the effect of UV irradiance on the decomposition of ozone. The decomposition rate obeyed first-order kinetics with respect to ozone concentration.

Figure 5 shows the effect of UV irradiance on the decomposition rate of ozone at $\text{pH } 5$. The decomposition rate was proportional to $\bar{I}$ in the range of $\bar{I} = 2\text{--}40 \text{ W} \cdot \text{m}^{-2}$. The activation energy in the presence of UV radiation was $16 \text{ kJ} \cdot \text{mol}^{-1}$ and was about one-fifth that without UV radiation.

Figure 6 shows the effect of pH value on the decomposition rate at 303 K . The exponent of $[\text{OH}^-]$ is much smaller than that in Eq. (8). In the presence of UV radiation, the decomposition in the liquid phase is initiated by Reaction (9) and is followed by Reaction (10). Therefore, OH^- ions do not play a key role in the decomposition reaction, and only weakly take part in the chain reaction by influencing the protonation equilibrium of O_2^- , O_3^- and HO^{2-} as shown by Reactions (2) and (3).

From the above, the decomposition rate of ozone in water in the presence of UV radiation is expressed by the following equation for $I = 2\text{--}40 \text{ W} \cdot \text{m}^{-2}$.

$$-d[\text{O}_3]/dt = k'[\text{OH}^-]^{0.07}[\text{O}_3]I \quad (13)$$

$$k' = 2.8 \exp(-16 \text{ kJ} \cdot \text{mol}^{-1}/RT) \quad (13a)$$

where the unit of concentration is $\text{mol} \cdot \text{m}^{-3}$.

Figure 7 shows the effects of UV irradiance and pH value on the decomposition rate of ozone at $[\text{O}_3] = 0.1 \text{ mol} \cdot \text{m}^{-3}$ and $T = 303 \text{ K}$. The overall decomposition rate of ozone is summarized by combining Eqs. (8) and (13).

$$\begin{aligned} -d[\text{O}_3]/dt = & k_a[\text{OH}^-]^{0.28}[\text{O}_3]^{1.5} \\ & + k_b[\text{OH}^-][\text{O}_3] + k'I[\text{OH}^-]^{0.07}[\text{O}_3] \end{aligned} \quad (14)$$

Equation (14) can be applied over the following ranges:

$$\begin{aligned} \text{pH} &= 2\text{--}9, \quad T = 279\text{--}303 \text{ K}, \quad I = 2\text{--}40 \text{ W} \cdot \text{m}^{-2}, \\ [\text{O}_3] &= 0.03\text{--}0.4 \text{ mol} \cdot \text{m}^{-3}. \end{aligned}$$

Fig. 3. Relationship between transmittance and average ozone concentration.

Fig. 4. Effect of UV irradiance on decomposition of ozone for $T = 283 \text{ K}$, $\text{pH} = 5$ and $[\text{O}_3] = 0.28\text{--}0.4 \text{ mol} \cdot \text{m}^{-3}$.

Fig. 5. Effect of UV irradiance on decomposition of ozone for $T = 279\text{--}303 \text{ K}$, $\text{pH} = 5$ and $[\text{O}_3] = 0.03\text{--}0.4 \text{ mol} \cdot \text{m}^{-3}$.

Fig. 6. Effects of pH value on decomposition rate at $T = 303 \text{ K}$.

Fig. 7. Effects of UV irradiance and pH value on decomposition rate of ozone at $T = 303\text{ K}$ and $[\text{O}_3] = 0.1\text{ mol} \cdot \text{m}^{-3}$.

2.2 Optimum UV irradiance

UV radiation accelerates ozone decomposition in the gas phase as well as in the liquid phase. If the UV irradiance is unnecessarily high, gaseous ozone is destroyed before it can be transferred into the liquid phase. Thus there is an optimum intensity for the UV radiation. Figure 8 shows a model reactor where refractory compounds are oxidized by the UV/ozone combination. The calculation is based on the following assumptions.

- (1) A bubble column is used as the reactor, and the gas and liquid phases are in plug flow and backmix flow, respectively.
- (2) The UV irradiance is constant anywhere in the reactor.
- (3) The decomposition rate of ozone in the gas phase is described by^{1,4)}

$$-dC/dt = \Phi_G a_G I C / (h\nu N_A) \quad (15)$$

where a_G is $302\text{ mol}^{-1} \cdot \text{m}^2$ for 253.7 nm .

- (4) The photolytic ozonation is carried out at $I \geq 1\text{ W} \cdot \text{m}^{-2}$. Then the first term on the right-hand side of Eq. (14) is neglected. Dissolved refractory compounds hardly influence the decomposition rate of ozone in the liquid phase.

The ozone concentrations in the gas and liquid phases are described by

$$-U_G dC/dx = K_G a (C - [\text{O}_3]H) + \varepsilon_G \Phi_G a_G I C / (h\nu N_A) \quad (16)$$

$$-(1 - \varepsilon_G)(k_b[\text{OH}^-] + k'[\text{OH}^-]^{0.07}I)[\text{O}_3] + K_G a \left(\int_0^{L_T} \frac{C}{L_T} dx - [\text{O}_3]H \right) = 0 \quad (17)$$

The increase in $K_G a$ due to decomposition in the liquid film is not appreciable in the range of $I \leq 100\text{ W} \cdot \text{m}^{-2}$. Equations (16) and (17) were solved

Fig. 8. Model reactor where refractory compounds are oxidized by UV/ozone combination.

analytically as shown in Appendix with the following boundary condition.

$$x=0; \quad C=C_i \quad (18)$$

The fractions of decomposed ozone are defined by

$$R_G = \frac{\text{(amount of ozone decomposed in the gas phase)}}{\text{(amount of ozone introduced into the reactor)}} \quad (19)$$

$$R_L = \frac{\text{(amount of ozone decomposed in the liquid phase)}}{\text{(amount of ozone introduced into the reactor)}} \quad (20)$$

The fraction of ozone discharged in the outlet stream is expressed by $(1 - R_G - R_L)$.

Figure 9 shows typical results of the simulation. Excessive intensity of UV radiation reduces the ozone concentration in the gas phase, and then decreases the mass transfer rate into the liquid phase. A decrease in gas velocity nominally improves ozone utilization, but always reduces the total amount of ozone decomposed in the liquid phase. These results suggest that the reactor should be divided into two zones, one each for O_3 absorption and UV radiation. Detailed methods for full-scale reactor design are left to future work.

Conclusion

The decomposition rate of ozone in water was studied in a flow reactor equipped with transparent quartz walls. The decomposition rate was proportional to the UV irradiance and the ozone concentration. The dependence on the OH^- ion concentration was very weak. These results suggest that the decomposition is initiated by Reaction (9). The overall decomposition rate of ozone was correlated with Eq. (14).

Fig. 9. Typical results of simulation. Calculation is carried out for pH=7, $T=293\text{ K}$, $L_T=5\text{ m}$, $U_G=10^{-2}\text{ m}\cdot\text{s}^{-1}$, $\varepsilon_G=0.031$, $H=3.23$ and $K_Ga=5.8\times 10^{-3}\text{ s}^{-1}$.

A preliminary simulation was carried out on the optimization of UV radiation in the reactor. An excessive increase in UV irradiance destroys ozone in the gas phase. As a result, ozone utilization in the liquid phase is hindered. The region for ozone absorption should be separated from that for UV radiation.

Appendix

Dimensionless variables are defined by

$$F_1 = C/C_i, \quad F_2 = [\text{O}_3]H/C_i, \quad z = x/L_T,$$

$$\alpha = K_GaL_T/U_G, \quad \beta = \varepsilon_G\Phi_Ga_GIL_T/(h\nu N_A U_G),$$

$$\gamma = (1 - \varepsilon_G)(k_b[\text{OH}^-] + k'[\text{OH}^-]^{0.07}I)L_T/(U_GH)$$

Then the solutions of Eqs. (16)–(18) are given as

$$F_1 = \left(1 - \frac{\alpha F_2}{\alpha + \beta}\right) \exp\{-(\alpha + \beta)z\} + \frac{\alpha F_2}{\alpha + \beta} \quad (\text{A-1})$$

$$F_2 = \frac{\alpha(\alpha + \beta)(1 - e^{-\alpha - \beta})}{(\alpha + \gamma)(\alpha + \beta)^2 + \alpha^2(1 - \alpha - \beta - e^{-\alpha - \beta})} \quad (\text{A-2})$$

The ozone consumption fractions, R_G and R_L , are derived as follows:

$$R_G = \frac{\beta}{\alpha + \beta} \left\{ 1 - e^{-\alpha - \beta} - \frac{\alpha}{\alpha + \beta} (1 - \alpha - \beta - e^{-\alpha - \beta}) F_2 \right\} \quad (\text{A-3})$$

$$R_L = \gamma F_2 \quad (\text{A-4})$$

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Nomenclature

a_G, a_L	= molar absorption coefficient of ozone at 253.7 nm in gas and liquid phase, respectively	$[\text{mol}^{-1}\cdot\text{m}^2]$
C	= molar concentration of ozone in gas phase	$[\text{mol}\cdot\text{m}^{-3}]$
C_i	= molar concentration of ozone in gas phase at $x=0$	$[\text{mol}\cdot\text{m}^{-3}]$

H	= Henry's constant, (molar concentration in gas phase)/(molar concentration in liquid phase)	$[-]$
h	= Planck's constant	$[\text{J}\cdot\text{s}]$
I_0, I_1	= UV irradiance defined in Fig. 2	$[\text{W}\cdot\text{m}^{-2}]$
$\bar{I}$	= logarithmic mean UV irradiance defined by Eq. (12)	$[\text{W}\cdot\text{m}^{-2}]$
K_Ga	= capacitance coefficient for mass transfer between bubble and liquid phase in bubble column	$[\text{s}^{-1}]$
k_a	= reaction rate coefficient defined by Eq. (8a)	$[\text{mol}^{-0.78}\cdot\text{m}^{2.34}\cdot\text{s}^{-1}]$
k_b	= reaction rate coefficient defined by Eq. (8b)	$[\text{mol}^{-1}\cdot\text{m}^3\cdot\text{s}^{-1}]$
k'	= reaction rate coefficient defined by Eq. (13a)	$[\text{mol}^{-0.07}\cdot\text{m}^{2.21}\cdot\text{s}^{-1}]$
L_T	= height of bubble column	$[\text{m}]$
l	= thickness of reactor	$[\text{m}]$
N_A	= Avogadro's number	$[\text{mol}^{-1}]$
$[\text{O}_3]$	= molar concentration of ozone in liquid phase	$[\text{mol}\cdot\text{m}^{-3}]$
$[\text{O}_3]_{lm}$	= logarithmic mean value of inlet and outlet ozone concentration	$[\text{mol}\cdot\text{m}^{-3}]$
$[\text{OH}^-]$	= molar concentration of OH^- ions	$[\text{mol}\cdot\text{m}^{-3}]$
R	= gas constant	$[\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}]$
R_G, R_L	= fraction defined by Eqs. (19) and (20), respectively	$[-]$
T	= temperature	$[\text{K}]$
t	= time	$[\text{s}]$
U_G	= superficial gas velocity	$[\text{m}\cdot\text{s}^{-1}]$
x	= height from gas distributor	$[\text{m}]$
ε_G	= gas holdup in bubble column	$[-]$
ν	= frequency of light	$[\text{s}^{-1}]$
Φ_G	= overall quantum yield for ozone decomposition in gas phase	$[-]$

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