Effect of Nitrite and Nitrate as the Source of OH Radical in the O₃/UV Process with or without Benzene[†]

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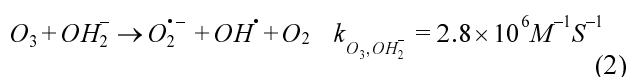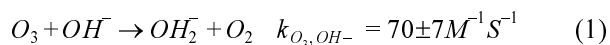
This study suggests the prediction model for the concentration variation of NO$_2^-$ and NO$_3^-$ along with the rate constants of all reactions during ozonation under UV radiation (O$_3$/UV process). While NO$_2^-$ was completely converted into NO$_3^-$ during the O$_3$-only process, the production of NO$_2$ radical or N$_2$O$_4$ was expected in the O$_3$/UV process. In addition, the quenching of OH radicals, by NO$_2$ radical in the O$_3$/UV process, resulted in regeneration of NO$_2^-$. However, the regeneration of NO$_2^-$ was not observed in the O$_3$/UV process in the presence of C$_6$H$_6$ where the concentrations of NO$_2^-$ and NO$_3^-$ were significantly reduced compared to in the process without C$_6$H$_6$. The pseudo-first order rate constants of all species were calculated with and without the presence of C$_6$H$_6$ to predict the variation of concentrations of all species during the O$_3$/UV process. It was suggested that NO$_2^-$ and NO$_3^-$ in the O$_3$/UV process can be more effectively removed from an aqueous system with an OH radical scavenger such as C$_6$H$_6$.

Key Words : Ozone, UV, OH radical, NO$_2^-$, NO$_3^-$

Introduction

Hydroxyl radical (OH radical, OH$^{\bullet}$) is a strong and nonselective oxidant that can be considered an alternative degrading agent for persistent organic compounds (POPs).[1] Photochemical processes are potent reactions to generate the OH radical by direct photolysis and photosensitized transformation involving photoexcited molecules such as hydrogen peroxide (H$_2$O$_2$), ozone (O$_3$), and ferrous (Fe^{2+}).[2,3] Although various radicals (^{1}O$_2$, ROO$^{\bullet}$, CO$_3^{-\bullet}$, HO$_2^{\bullet}$, Cl$_2^{-\bullet}$, and NO$_2^{\bullet}$) are generated during the photochemical process, OH radical plays the most significant role as an oxidant to elevate the degradation efficiency of many inorganic and organic compounds.[3-6]

Ozonation, which is the producing process the OH radical through Eqs. 1 and 2[7-10], is also an effective treatment method for trace organic contaminants in water. However, the generation of OH radical in the O$_3$-only process is not effective due to the slow rate of Eq. 1 in regard to enhancing the oxidation of pollutants by OH radical.[11,12]

$$O_3 + OH^- \rightarrow OH_2^- + O_2 \quad k_{O_3,OH-} = 70\pm7 M^{-1}S^{-1} \quad (1)$$

$$O_3 + OH_2^- \rightarrow O_2^{\bullet-} + OH^{\bullet} + O_2 \quad k_{O_3,OH_2^-} = 2.8\times10^6 M^{-1}S^{-1} \quad (2)$$

Although ozonation is effective for microbial disinfection and the oxidation of trace contaminants, O$_3$ plays a limited role as an oxidant to degrade recalcitrant compounds compared to OH radical due to the lower oxidizing power of O$_3$.[13] Therefore, the enhancement of the concentration of

OH radical in the ozonation system is an effective approach to improve the degradation efficiency of contaminants. Rosehfeldt *et al.*[14] reported that the generation of the OH radical was greater in O$_3$/H$_2$O$_2$ than in O$_3$-only process and the formation of OH radical was possible only after the first-order decay of O$_3$ in the O$_3$/H$_2$O$_2$ process.[15] Ozonation under UV radiation (O$_3$/UV) provided various pathways for OH radical formation by the phlotolysis of O$_3$ and generally induced a greater degradation efficiency of nitrobenzene than simply the O$_3$-only process.[16,17]

The photolysis of nitrate (NO$_3^-$) in aqueous solution can be considered as one of the sources of the OH radical.[18-20] NO$_3^-$ being involved with the electron acceptor in biological systems is thermodynamically and biologically very stable and soluble. It is well known that nitrite (NO$_2^-$) is oxidized to NO$_3^-$ by nitrobacter in soil and water systems.[21,22] The oxidation of NO$_2^-$ to NO$_3^-$ is possible by microbial reaction or O$_3$.[23] Furthermore, the generation of OH radical by the photolysis of NO$_3^-$ in UV-B range[21,22] strongly suggests a possible chain reaction between NO$_2^-$ and NO$_3^-$ in aqueous system. The chain reaction can be because of the role of NO$_3^-$ as the source of OH radical. Therefore, the pathway for the OH radical in the O$_3$/UV system during the chain reaction between NO$_2^-$ and NO$_3^-$ needs to be explained in further detail.

In this research, we focussed on examining the overall reaction path along with the role of both NO$_2^-$ and NO$_3^-$ in the generation of OH radical in O$_3$/UV process. We further suggested a model, with which we can predict the rate constant for the oxidation of NO$_2^-$. In order to suggest the model of NO$_2^-$ and NO$_3^-$ in O$_3$/UV system, C$_6$H$_6$ was used as the scavenger of the OH radical.
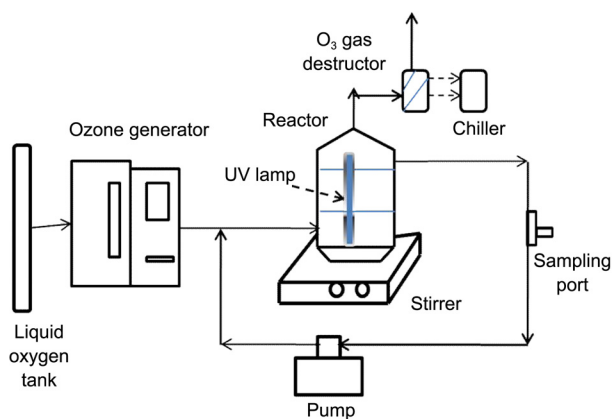
Figure 1. Schematic representation of the O_3/UV system.

Figure. 2. The influence of O_2 flow rate to generate dissolved O_3 concentration and O_3 flow rate.

Experimental

Chemicals & Experimental Setup. NO_2^- and NO_3^- was prepared by diluting a 1000 mg L^{-1} (standard solution for ion chromatography, Fluka) in Nanopure deionization water (R = 18 M cm^{-1}; Barnstead Co., Ltd., Dubuque, IA). Benzene (C_6H_6) from Merck (99.9%) from Merck was HPLC or analytical reagent grade.

O_3 was produced from pure liquid oxygen (O_2, 99.999%) by the O_3 generator (Sewang C.E.Tech., Korea). O_3/UV system (Fig. 1) was semi-circulation type and O_3 was mixed with the treated water in line before being provided to the reactor. Gas phase O_3 unreacted from reactor was wasted through the O_3 gas destructor, during which the increased thermal state was controlled by the chiller. UV-C lamps (13 W, low pressure UV lamp, Sankyo) in quarts cell were installed in the reactor (10 cm × 10 cm × 40 cm), and their intensity (5.2 mW cm^{-2}) was measured by a VLX-3W radiometer (Cole-Parmer, USA).

Analysis. Gas phase O_3 concentration (%, wt) was determined by the O_3 analyzer (model H1, In USA Inc). Dissolved O_3 concentration was calculated by O_3 application rate (Eq. 3) based on absorbance measured with a UV-Visible spectrophotometer (HS-3300, Humus, Korea) at 254 nm.[24,25]

$$v_{EOP} = \frac{3600(A\,G_A M)}{\varepsilon l} \qquad (3)$$

where V_{EOP} = O_3 application rate (g h^{-1}), A = absorbance at 254 nm; G_A = volumetric flow rate of the anodic gases (O_2 or O_3) ($dm^3 s^{-1}$); e = 3024 $dm^3 mol^{-1} cm^{-1}$ is the O_3 aborptivity at 254nm in the gas phase; l = optical path length (0.63 cm) and M = ozone molecular weight (48 g mol^{-1}).

Figure 2 shows the concentration relationship between dissolved O_3 and gas phase O_3, which was formed by the conversion of liquid O_2 through an ozone generator used in this study. O_3 flow rate in Fig. 2, which represented the gas phase of O_3 from the conversion of O_2, increased with the increase of O_2 flow rate. However, the dissolved O_3 concentration flatted off at an O_2 flow rate of more than 20 L min^{-1}. It is assumed that the self reaction of O_3 occurred with
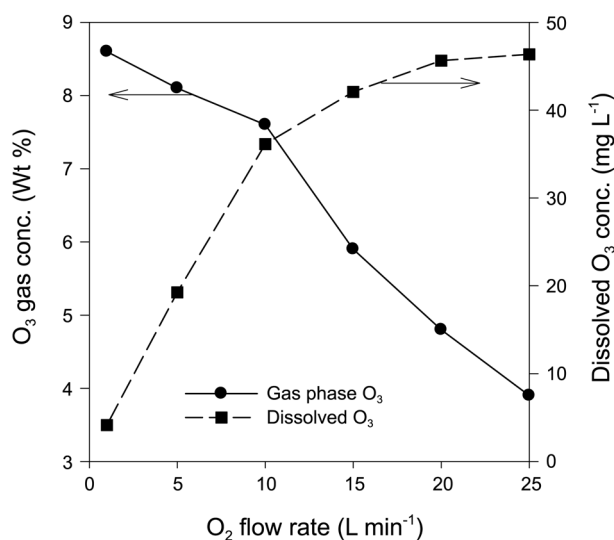
an increase of O_3 concentration. Because the reaction between O_3 and other compounds occurred in 30 sec^{15}, O_3 was injected continuously during the reaction time in this study. In addition, the concentration of O_3 during the reaction was maintained by the lowest level (4.10 × 10^{-5} M), which was selected in order to induce the low reaction rate.

NO_2^- and NO_3^- were measured with a DX-120 ion chromatograph (Dionex) using a Dionex Ion Pac AS14 column with a mixture of 3.5 mM Na_2CO_3 and 1 mM $NaHCO_3$ as an eluent. N_2O_4 or NO_2 radical were recognized by the difference between the initial concentration of NO_2^- and the sum of NO_2^- and NO_3^- using the results of previous studies.

C_6H_6, which was extracted via solid phase extraction by C-18 solid cartridges (Waters, USA), was analyzed by gas chromatography (Hewlett Packard 6890) and a mass selective detector (Hewlett Packard 5973) with non-polar capillary column (HP-Ultra 1, 12 m × 0.2 mm × 0.33 μm). The sample (2 μL) was injected into the GC at 250 °C with the splitless condition. The temperature was programmed 70 to 120 °C at a rate of 10 °C min^{-1} and held for 3 min at 180 °C. The solution pH was measured using a model 52A pH analyzer (Orion, Reno, NV).

Results and Discussion

Kinetic Study. Table 1 shows the pseudo-first order rate constants of the NO_2^- degradation in O_3-only, and O_3/UV with or without C_6H_6. NO_2^- was not degraded by photolysis (UV-only) and the degradation rate of NO_2^- in O_3-only and O_3/UV reactions was not significantly different. Interestingly, the rate constant was much smaller in O_3/UV reaction with C_6H_6 compared to the rate constant in others related to O_3 without C_6H_6.

As shown in Table 1, the kinetics for the NO_2^- degradation conformed to the pseudo-first rate model in O_3-only and O_3/UV reactions. The result indicates that the concentration of

Table 1. Pseudo-first order rate constants and R^2 values of NO_2^- degradation for initial 10 min of various reactions ($[NO_2^-]_0$: 3 mM, $[C_6H_6]_0$: 3 mM, $[O_3]$: 0.041 mM, pH: 6.5 ± 0.3).

Reaction type	k_1 [min⁻¹]	R^2
O_3-only	0.246 ± 0.013	0.989 ± 0.002
UV-only	0.001 ± 0.000	0.450 ± 0.037
O_3/UV	0.249 ± 0.004	0.972 ± 0.011
O_3/UV with C_6H_6	0.166 ± 0.006	0.977 ± 0.009

NO_2^- was the rate determining factor. In other words, the concentration of dissolved O_3 can be considered as constant in the experiment condition presented in Table 1. Therefore, the degradation rate model of NO_2^- in the reactions related O_3 was induced, such as Eq. 4.

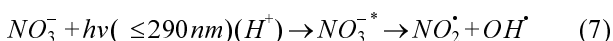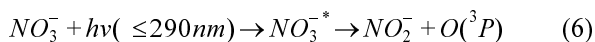$$\frac{d[NO_2^-]}{dt} = -k_{2,1}[O_3][NO_2^-] = k_1[NO_2^-] \qquad (4)$$

where $k_{2,1}$ and k_1 was the second-order rate constant $[M^{-1} min^{-1}]$ and pseudo-first order rate constant $[2.78 \times 10^{-1} min^{-1}]$, and $[O_3]$ and $[NO_2^-]$ were the concentrations [M] of O_3 and NO_2^-, respectively.

Transformation of NO_2^- in O_3-only and O_3/UV Reactions. Figure 3 shows the production extents of NO_3^- during degrading NO_2^- by O_3-only reaction. As shown in Fig. 3(a), the complete mass balance between NO_2^- and NO_3^- was accomplished in O_3-only reaction where all the NO_2^- was converted to NO_3^- over 10 min reaction time. The complete conversion of NO_2^- to NO_3^- by O_3 was previously revealed in a few studies.[22,26] By the result from Fig. 3, it can be assumed that NO_2^- was degraded by O_3, such as Eq. 5.

$$NO_2^- + O_3 \rightarrow NO_3^- + O_2 \qquad (5)$$
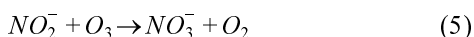
O_3 gas in the reactor was constantly provided during the reaction period where the dissolved O_3 concentration was calculated to be 4.10×10^{-5} M. Therefore, $k_{2,1}$ in Eq. 4 was determined as $6.8 \times 10^3 M^{-1} min^{-1}$ based on the dissolved concentration.

As shown in Fig. 3(b), the degradation of NO_2^- in O_3/UV reaction did not produce only NO_3^- but other compounds as well, which was recognized as the concentration gap between NO_2^- and NO_3^-. Some studies reported that NO_3^- can be photo-degraded in the wavelength less than 290 nm, such as Eqs. 6 and 7.[16-18,27]
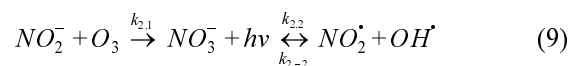
$$NO_3^- + hv(\leq 290nm) \rightarrow NO_3^{-*} \rightarrow NO_2^- + O(^3P) \qquad (6)$$

$$NO_3^- + hv(\leq 290nm)(H^+) \rightarrow NO_3^{-*} \rightarrow NO_2^{\bullet} + OH^{\bullet} \qquad (7)$$

This shows that NO_2 radical and NO_2^- can also be generated by the photolysis of NO_3^- in the O_3/UV process. However, the regeneration of NO_2^- in O_3/UV was not attained in this reaction, which was implicated by similar NO_2^- degradation rate constants between O_3-only and O_3/UV reactions (Table 1). Therefore, the difference between NO_2^- and NO_3^- in Fig. 3(b) ($|NO_2^--NO_3^-|$) can be represented as NO_2 radical ($NO_2^{\bullet}$) as shown in Eq. 7. NO_2 radical is a very strong one-electron oxidant in aqueous solution[28],

(a)

(b)
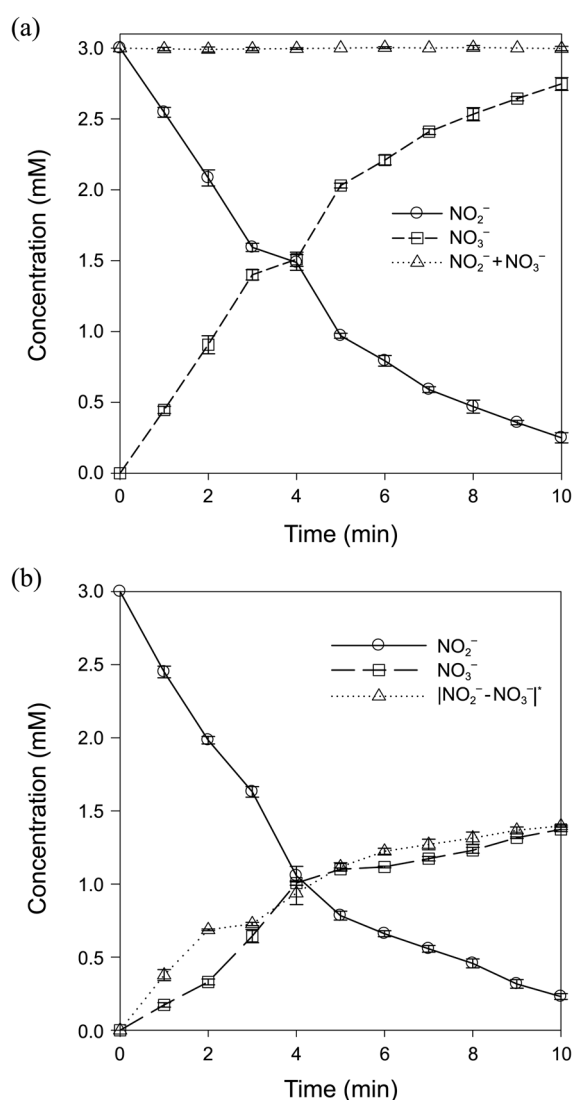
Figure 3. Transformation from NO_2^- to NO_3^- and others in (a) O_3-only and (b) O_3/UV reactions ($[NO_2^-]_0$: 3 mM, pH: 6.5 ± 0.3). * $|NO_2^--NO_3^-| \stackrel{.}{=} NO_2$ radical

which plays the role of the OH radical scavenger, as shown by Eq. 8.[29] In particular, Eq. 8 occurs in the bulk solution in the deionized water.[30] It is noted that the photolysis of NO_3^- accompanies the generation reaction as well as the sink reaction of OH radical.

$$NO_2^{\bullet} + OH^{\bullet} \stackrel{k_{2,-2}}{\rightarrow} HNO_3 \quad k_{2,-2} = 1.3 \times 10^9 M^{-1}S^{-1} \qquad (8)$$
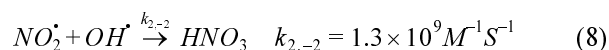
Interestingly, the change trends of $[NO_3^-]$ were identical with those of $[NO_2$ radical$]$, implicating that the degradation and generation reactions of NO_3^- in O_3/UV reaction were accomplished with similar rates. Based on the results, the behaviour of NO_2^- in the O_3/UV process can be explained as shown in Eq. 9, where the rates were comprised as Eq. 4, 10, and 11.
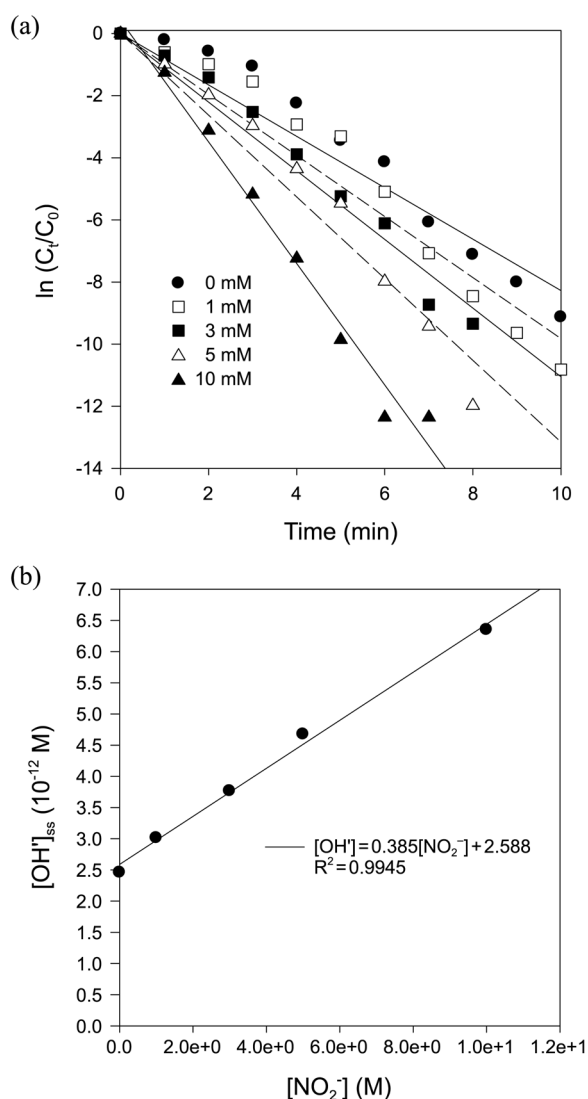
$$NO_2^- + O_3 \stackrel{k_{2,1}}{\rightarrow} NO_3^- + hv \underset{k_{2,-2}}{\overset{k_{2,2}}{\leftrightarrow}} NO_2^{\bullet} + OH^{\bullet} \qquad (9)$$

(a)

(b)

Figure. 4. (a) Effect of NO_2^- to degrade C_6H_6 in regard to the pseudo-first order kinetic model (b) relationship of [OH·] and [NO_2^-] in the O_3/UV process ([C_6H_6]$_0$: 3mM, pH: 6.5 ± 0.3).

$$\frac{[NO_3^-]}{dt} = -k_{2,2}[NO_3^-][hv] + k_{2,-2}[NO_2^\cdot][OH^\cdot] + k_{2,1}[NO_2^-][O_3]$$

$$= -k_2[NO_3^-] + k_{-2}[NO_2^\cdot] + k_1[NO_2^-] \qquad (10)$$

$$\frac{[NO_2^\cdot]}{dt} = -k_{2,-2}[OH^\cdot][NO_2^\cdot] + k_{2,2}[NO_3^-][hv]$$

$$= k_{-2}[NO_2^\cdot] + k_2[NO_3^-] \qquad (11)$$

where $k_{2,1}$, $k_{2,2}$, and $k_{2,-2}$ [M^{-1} min^{-1}] are the second-order rate constants for each reaction in Eq. 9, respectively. Also, k_1, k_2, and k_{-2} [min^{-1}] are the pseudo-first order rate constants corresponding to $k_{2,1}$, $k_{2,2}$, and $k_{2,-2}$, respectively.

Determination of OH Radical in O_3/UV Process. As shown in Eq. 7 and 8, the chain reactions of NO_2^- and NO_3^- in the O_3/UV process play both roles to source and sink the OH radical. Therefore, the behaviour of the OH radical should be ascertained for estimating the fate of NO_2^- in the process.

C_6H_6, which has a great rate constant with OH radical (6×10^9 $M^{-1}s^{-1}$)[31], was used as a model compound in order to induce competition reactions for OH radical with NO_2^-. Fig. 4(a) shows that the degradations of C_6H_6 in O_3/UV process were well conformed to the pseudo-first order rate, as shown by Eq. 12, with R^2 values of over 0.9745, which increased with the increase of NO_2^- addition in solution. Therefore, the concentration of C_6H_6 was the rate determining factor and the concentration of OH radical could be regarded as the constant.

$$\frac{[C_6H_6]}{dt} = -k_{benz}[OH^\cdot][C_6H_6] = -k_{exp}[C_6H_6] \qquad (12)$$

where k_{exp}[min^{-1}] was represented as the rate constant observed in the degradation experiment of C_6H_6, and k_{benz} was 6×10^9 $M^{-1}S^{-1}$.

Using Eq. 12 and the known value of k_{benz}, OH radical concentration was calculated. Because the relationship between [OH·] and [NO_3^-] has the linearity as shown in Fig. 4(b), [OH·] and k_{-2} (=$k_{2,-2}$[OH·], Eq. 10 and 11) at [NO_2^-]$_0$ (3 mM) can be calculated with the regression equation, which are 3.74×10^{-12} M and 2.92×10^{-1} min^{-1}.

Based on the k_{-2} values, the differential equations (Eqs. 4, 10 and 11), and Eq. 13, k_2 value, which should be larger than k_{-2} by the experimental data, is $(3.20 \pm 0.0045) \times 10^{-1}$ min^{-1}.

$$[NO_2^-] + [NO_3^-] + [NO_2^\cdot] = [NO_2^-]_0 \qquad (13)$$

Where [NO_2^-]$_0$ is the initial concentration of NO_2^-. By the calculations, the changes of NO_2^-, NO_3^-, and NO_2 radical in the O_3/UV reaction were modelled to Eqs. 14, 15, and 16 with the function of time, respectively.

$$[NO_2^-] = [NO_2^-]_0 e^{-0.278t} \qquad (14)$$

$$[NO_3^-] = 0.612 \times [NO_2^-]_0 (1 - e^{-0.278t}) \qquad (15)$$

$$[NO_2^\cdot] = 0.671 \times [NO_2^-]_0 (1 - e^{-0.278t}) \qquad (16)$$

Effect of C_6H_6 in O_3/UV Reaction. As shown in Fig. 5, C_6H_6 completely degraded in 8 min of O_3/UV reaction, when the production portion of |NO_2^--NO_3^-| surpassed that of NO_3^-. Fig. 5 also showed that the accumulation of NO_3^- began after degrading C_6H_6 completely. It is possible that the chain reaction between NO_2^- and NO_3^- should be achieved via the production of other nitrogen species which were represented as |NO_2^--NO_3^-| in this study. In addition, the degradation rate constant of NO_2^- reduced with C_6H_6 during the O_3/UV reaction (Table 2). Because the species of |NO_2^--NO_3^-| were initialized from the degradation of NO_3^-, the transformation rate of NO_2^- to NO_3^- may have nothing to do with the presence of C_6H_6 in solution. This indicates that C_6H_6 induced the competitive reaction to OH radical with NO_2^-.

Some studies say that NO_2^- may be regenerated through the degradation of N_2O_4 which was recombined by NO_2 radical (Eq. 17 and 18).[30,32]

$$2NO_2^\cdot \rightarrow N_2O_4 \qquad (17)$$

Table 2. Pseudo-first order rate constants and R^2 values of C$_6$H$_6$ and NO$_2^-$ degradation for each stage of O$_3$/UV with C$_6$H$_6$ ([NO$_2^-$]$_0$: 3 mM, [C$_6$H$_6$]$_0$: 3 mM, [O$_3$] : 0.041 mM, pH: 6.5 ± 0.3)

	0-8 min		8-15 min		0-15 min	
	k_1(min^{-1})	R^2	k_1(min^{-1})	R^2	k_1(min^{-1})	R^2
NO$_2^-$	0.175 ± 0.010	0.988 ± 0.005	0.239 ± 0.005	0.949 ± 0.012	0.166 ± 0.006	0.977 ± 0.009
C$_6$H$_6$	0.262 ± 0.005	0.992 ± 0.004	–	–	–	–
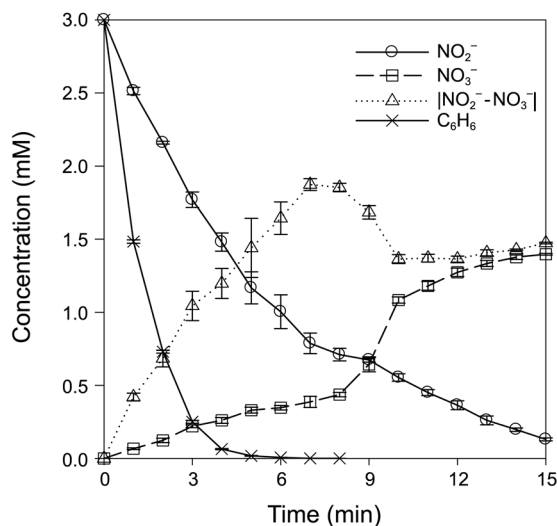
Figure 5. Transformation from NO$_2^-$ to NO$_3^-$ and others in the O$_3$/UV reactions with C$_6$H$_6$ ([NO$_2^-$]$_0$: 3 mM, pH: 6.5 ± 0.3).

$$N_2O_4 + H_2O \rightarrow HNO_2 + HNO_3 \qquad (18)$$
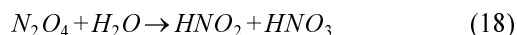
When C$_6$H$_6$ and NO$_2^-$ competed in the O$_3$/UV reaction, the cycle reactions of NO$_2^-$ may be modified as shown in Fig. 6. Treinin and Hayon[32] showed that most of the NO$_2$ radical was converted to N$_2$O$_4$ at an equilibrium state. However, the rate constant of Eq. 16 (4.5 × 10^8 M^{-1}s^{-1})[30] was slower than that of the reaction between NO$_2$ radical and OH radical (1.3 × 10^9 M^{-1}s^{-1}). Since the reaction of NO$_2$ radical and OH radical was inhibited due to scavenging of the OH radical by C$_6$H$_6$, |NO$_2^-$-NO$_3^-$| presented in Fig. 5 may exist in the form of N$_2$O$_4$ rather than NO$_2$ radical. Therefore, the regeneration of NO$_2^-$ and NO$_3^-$ was produced by the hydrolysis of N$_2$O$_4$ (Eq.18) during the reaction of C$_6$H$_6$ and OH radical, of which the concentration was insignificant as shown in Fig. 6. It implicates that the O$_3$/UV system may be a removal system of NO$_2^-$ and NO$_3^-$ in aqueous system due to phase change. According to Fig. 6(b), the rate models of NO$_2^-$, NO$_3^-$, and N$_2$O$_4$ were assumed by Eqs. 19, 20, and 21

$$\frac{[NO_2^-]}{dt} = -k_1[NO_2^-] + k_4[N_2O_4] \qquad (19)$$

$$\frac{[NO_3^-]}{dt} = -k_2[NO_3^-] + k_1[NO_2^-] + k_4[N_2O_4] \qquad (20)$$

$$\frac{[N_2O_4]}{dt} = k_2[NO_3^-] - k_4[N_2O_4] \qquad (21)$$

where k$_4$ [min^{-1}] was the first order rate constant of N$_2$O$_4$ abatement in Eq. 17. By solving the differential equations
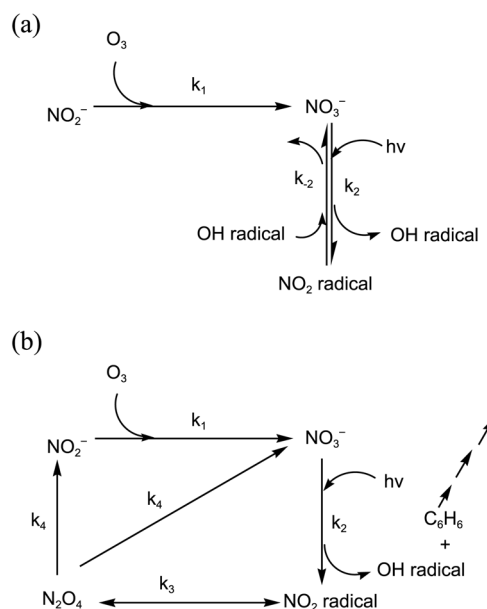
Figure. 6. Cycle reactions of NO$_2^-$, NO$_3^-$, NO$_2$ radical, and N$_2$O$_4$ in O$_3$/UV reaction (a) with and (b) without C$_6$H$_6$.

(Eqs. 18, 19, 20) and using mass balance equation (Eq. 21), k$_4$ was calculated as (0.66 ± 0.003) × 10^{-1} min^{-1} and the models in the O$_3$/UV reaction with C$_6$H$_6$ were made for the changes of [NO$_2^-$], [NO$_3^-$], and [N$_2$O$_4$] (Eqs. 23,24,25).

$$[NO_2^-] + [NO_3^-] + [N_2O_4] = [NO_2^-]_0 \qquad (22)$$

$$[NO_2^-] = [NO_2^-]_0 e^{-0.278t} \qquad (23)$$

$$[NO_3^-] = 0.192[NO_2^-]_0(1 - e^{-0.278t}) \qquad (24)$$

$$[N_2O_4] = 0.192[NO_2^-]_0(1 - e^{-0.278t}) \qquad (25)$$

Comparing Eq. 14 with Eq. 23, the degradation rate of NO$_2^-$ decreased by the presence of C$_6$H$_6$. This was caused by the regeneration of NO$_2^-$ by the hydrolysis of N$_2$O$_4$, of which the rate was more gentle compared to that of the reduction of NO$_3^-$, resulting in the accumulation of N$_2$O$_4$ (or NO$_2$ radical) as shown in Fig. 5. As a result, the chain reactions initiated from NO$_2^-$ in O$_3$/UV significantly changed by the addition of C$_6$H$_6$, depending on the OH radical generated in the reaction.

Conclusion

In this paper, the reversible reaction system of NO$_2^-$, NO$_3^-$, and NO$_2$ radical/N$_2$O$_4$ in the O$_3$/UV process with rate constants of all reactions involved was shown. It was found

that the NO_2 radical in the O_3/UV process quenched the OH radical produced during the degrading reaction of NO_3^-. This means that the NO_2^- or NO_3^- was not appropriate for boosting up the generation of OH radical in the O_3/UV process. However, this process became an effective degrading method by introducing C_6H_6, which had high affinity to OH radical, under the presence of NO_2^- or NO_3^-. Furthermore, it is possible that NO_2^- or NO_3^- in solution is changed to N_2O_4 from liquid phase to gas in open state. Therefore, the competitive reaction of NO_2^- (NO_3^-) and materials affinitive with OH radical in O_3/UV process can be effective method to remove NO_2^- and/or NO_3^- as well as to mineralize recalcitrant pollutants in aqueous system.

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