Photocatalytic degradation of mono-, di- and trinitrophenol in aqueous TiO$_2$ suspension

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Abstract

Three mononitrophenol compounds (2-, 3- and 4-) 2,4-dinitrophenol and picric acid (2,4,6-trinitrophenol) were photocatalytically degraded in aqueous TiO$_2$ suspension. Among three mononitrophenol compounds the degradation rate of 4- and 2-nitrophenol were larger than that of 3-nitrophenol. The degradation rate decreased with the number of nitro group substituents. This reactivity follows Hammett law with regard to the effect of nitro group on phenolic functionality. Several polyhydroxylated aromatic intermediates were identified for mono- and dinitrophenol which indicated that the degradation started by the substitution of hydrogen and nitro groups by hydroxyl radical. Organic acid intermediates were identified besides aromatic compounds, among which formic and acetic acids were formed in the largest quantity. It was suggested for the transformation of nitro group that the formation ratio of NO$_3^-$ and NH$_4^+$ reflected the degradation mechanism of starting nitrophenolic compound.

Keywords: Photocatalysis; Titania; Nitrophenol

1. Introduction

The photocatalytic degradation of toxic compounds in aqueous medium provides a new method for waste water treatment. It has several advantages over conventional oxidation processes such as the complete mineralization of pollutant, utilization of near-UV light and no addition of chemicals. This method has been studied intensively over the past two decades. The recent works in this field were reviewed in several review articles [1–4]. It has been proved by those works that many water soluble chemicals from various industries can be degraded photocatalytically. However, more investigations on photocatalytic process of various pollutants are required before the practical application. This report is to study the photocatalytic degradation process of several nitrophenolic compounds [5,6].

Picric acid is used for the production of explosive materials, agrochemicals, coloring agents and so on. Dinitrophenol (2,4-) is a preservative and intermediate for coloring agent. Mononitrophenol is a starting material of many chemical products. It is reported that mononitrophenol can be formed as a degradation product

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of herbicide nitrofen when it is exposed to sunlight [7]. Because of their high water solubilities, those compounds are often found in the waste water from various industries. Biological methods are not very effective on the degradation of these compounds [8,9]: therefore there is a strong demand for the development of alternative methods.

2. Experimental

The TiO_2 used throughout the experiment is TP-2 anatase, supplied from Fujititan Co. The specific surface area is 17.3 m^2/g. The high photocatalytic activity of this grade was shown in our previous paper [10]. Other chemicals were reagent grade commercial products except 2-nitrohydroquinone which was synthesized following the procedure reported in the literature [11].

Degradation experiments were carried out using TiO_2 in suspension. Seventy-five mg of TiO_2 powder was suspended in 25 ml of sample solution in a Pyrex glass bottle by stirring magnetically. The bottle was illuminated by a 500 W super-high pressure mercury lamp through a water filter. The light intensity was 18 mW cm^{-2} in the 330–390 nm region. After the illumination the suspension was filtered and the filtrate was subjected to analysis. Nitrophenolic compounds were analyzed by a HPLC with a UV detector and reverse-phase ODS column. Most of intermediate products were analyzed by a HPLC with a multi-wavelength UV-VIS detector Jasco MD-90, which allows the measurement of absorption spectrum of compound detected by retention time. Hence the intermediate compounds were confirmed by both the retention time and absorption spectrum. Organic ion was detected by a background-suppressing type ionchromatograph Yokogawa IC-7000. NO_3^-, NO_2^- and NH_4^+ were analyzed by ionchromatograph consisting of a Jasco 880 pump and a conductivity detector Shodex CD-4. TOC (total organic carbon) was measured by a Shimadzu

TOC-500. UV-VIS absorption spectrum was measured by a Jasco 670 spectrophotometer.

3. Results

Degradation of mononitrophenol (2-, 3- and 4-), 2,4-dinitrophenol and picric acid, in 2×10^{-4} mol l^{-1} solution by illumination was negligibly small in the absence of TiO_2. The addition of TiO_2 accelerated the degradation of all these compounds considerably. Among three mononitrophenol compounds the disappearance rates of 4- and 2-nitrophenol were larger than that of 3-nitrophenol (Fig. 1), in agreement with Sclafani et al.'s result [5]. The disappearance rates of nitrophenolic compounds with different numbers of nitro groups were compared in Fig. 2 and their TOC elimination rates were in Fig. 3 for the initial concentrations of 10^{-4} and 10^{-3} mol l^{-1}. Degradation rate expressed as the amount of compound degraded for fixed time was larger for the higher initial concentration. All these nitrophenolic compounds of 2×10^{-4} mol l^{-1} disappeared before 90 min and their TOC's were eliminated within 3 h. Although these values do not have absolute meaning, they show relative degradability among different nitrophenolic compounds. Degradation rates were in the order: phenol > 4-nitrophenol > 2,4-dinitrophenol > picric acid. This order agrees
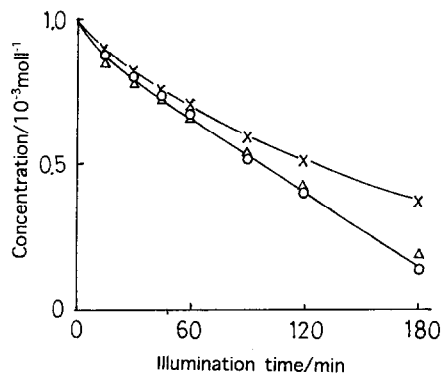

Fig. 1. Comparison of photocatalytic degradations of three mononitrophenol compounds. O 4-nitrophenol, △ 2-nitrophenol, × 3-nitrophenol.
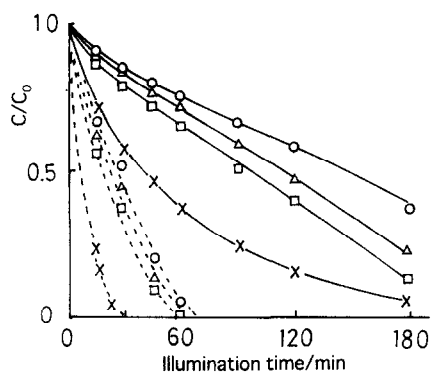
Fig. 2. Photocatalytic degradations of picric acid, 2,4-dinitrophenol and 4-nitrophenol. O Picric acid, △ 2,4-dinitrophenol, □ 4-nitrophenol, × phenol. Initial concentration: ——— 10^{-3} mol l^{-1}, ··· 2×10^{-4} mol l^{-1}.

Fig. 4. Formations of hydroquinone from 4-nitrophenol, catechol from 2-nitrophenol and resorcinol from 3-nitrophenol. O hydroquinone, △ catechol, × resorcinol. Initial concentration: 10^{-3} mol l^{-1}.

with an increasing number of nitro groups. The difference in the rates between disappearance and TOC elimination indicates the formation of photocatalytically less degradable intermediate compounds than starting materials.

Several aromatic intermediate compounds from nitrophenolic compounds were identified and the formation curves for some of them are shown in Figs. 4 and 5. From 4-nitrophenol, hydroquinone and 4-nitrocatechol were formed in nearly equal amounts, whereas nitrohydroquinone and smaller amount of catechol were formed from 2-nitrophenol, and nitrohydroquinone and far smaller amount of resorcinol were formed from 3-nitrophenol. From 2,4-di-
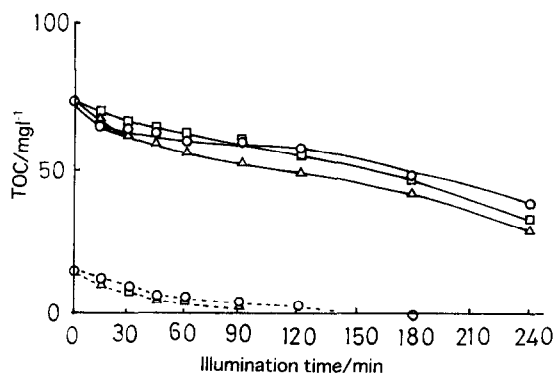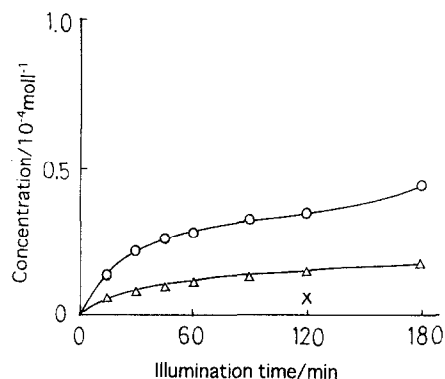
nitrophenol, 4-nitrocatechol and 2-nitrohydroquinone were formed. Unfortunately no aromatic intermediate was identified for picric acid. All the aromatic intermediates identified were shown in Fig. 6. Numbers in parentheses are the maximum concentrations formed from initial concentration of 2×10^{-4} mol l^{-1}. UV absorption spectrum showed that as the degradations of three mononitrophenol compounds and 2,4-dinitrophenol proceeded, intermediate compounds having an absorption at the longer wavelength than starting compounds were formed (Fig. 7), and subsequently degraded by the further illumination. Among aromatic intermedi-
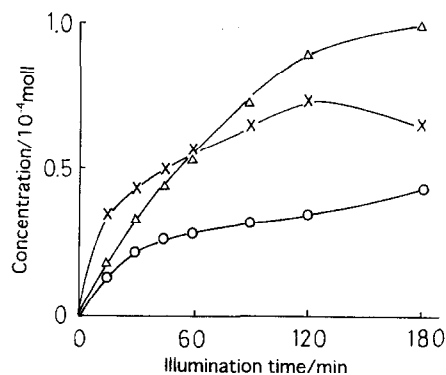

Fig. 3. TOC elimination from the solutions of piric acid, 2,4-dinitrophenol and 4-nitrophenol. O picric acid, △ 2,4-dinitrophenol, □ 4-nitrophenol, × phenol. Initial concentration: — 10^{-3} mol l^{-1}, ··· 2×10^{-4} mol l^{-1}.

Fig. 5. Formation of hydroxylated compound substituted at para from mononitrophenol. △ nitrohydroquinone from 2-nitrophenol, × nitrohydroquinone from 3-nitrophenol, O hydroquinone from 4-nitrophenol.

Fig. 7. Absorption spectrum of 2-nitrophenol after the illumination for different times. Initial concentration: 2×10^{-4} mol l^{-1}. 1. 0 min, 2. 15 min, 3. 30 min, 4. 45 min.

($< 10^{-5}$ mol l^{-1} from 2×10^{-4} mol l^{-1} of starting material). Larger molecules such as muconic and maleic acids found in other oxidative degradation of aromatic compounds [14,15] were below analytical limit. The concentration of formic acid formed was larger than that of acetic acid. But formic acid disappeared quickly, while acetic acid degraded slowly. The order of the formation rates of acetic acid from three nitrophenolic compounds was in agreement with that of disappearance rates of these compounds, whereas that of formic acid was in the reverse order of it (Fig. 8). Final degradation products were CO_2, NO_3^-, NO_2^- and NH_4^+. The amount of NO_3^- were plotted against illumination time
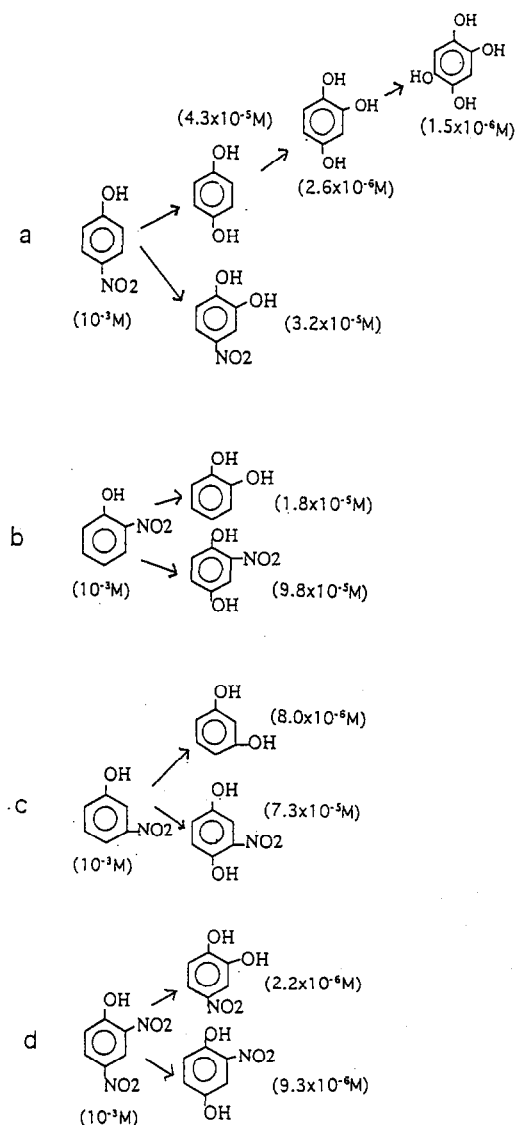

Fig. 6. Formation of hydroxylated armatic intermediates from mononitrophenol (2-, 3- and 4-) and 2,4-dinitrophenol. (a) 4-nitrophenol, (b) 2-nitrophenol, (c) 3-nitrophenol, (d) 2,4-dinitrophenol.

ates identified (Fig. 6), nitrohydroquinone matches this wavelength. However the formation of condensation products which have absorption at the longer wavelength can not be excluded [5,12,13]. Formic and acetic acids were formed as other intermediates besides aromatic compounds (Fig. 8). Other organic acids such as glycolic, glyoxylic and malonic acids were also formed, but their concentrations were smaller
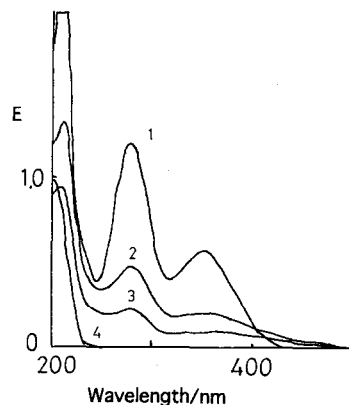
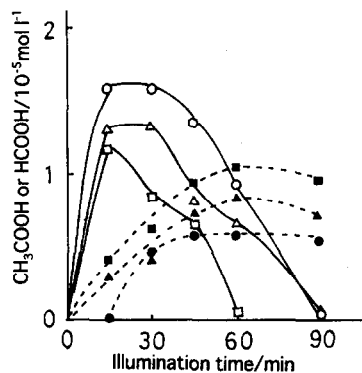

Fig. 8. Formation of formic and acetic acids from three nitrophenolic compounds. ○,● picric acid, △,▲ 2,4-dinitrophenol, □,■ 4-nitrophenol, — ○,□,△ formic acid, · · · ●,■,▲ acetic acid.
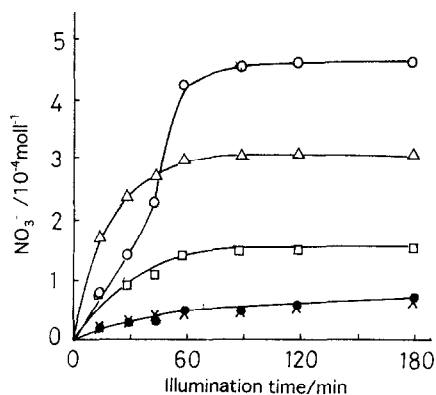
Fig. 9. Formation of NO_3^- from five nitrophenolic compounds. ○ picric acid, △ 2,4-dinitrophenol, □ 4-nitrophenol, ● 2-nitrophenol, × 3-nitrophenol.

in Fig. 9. It is to be noted that the formation rate of NO_3^- from picric acid is relatively slow when it is taken into consideration that picric acid possesses three nitro groups. The amounts of NO_2^- formed from all the compounds were very small ($< 10^{-5}$ mol l^{-1}). The rest of nitrogen formed NH_4^+.

4. Discussion

Picric acid is the least degradable among the four nitrophenolic compounds as shown in Figs. 2 and 3. In our previous paper [16] and others [17] it was reported that photocatalytic degradation rate of aromatic compound is affected by functional groups attached to the aromatic ring, and particularly nitro substituent suppresses the degradation. The effect of the functional group is based on its eletronegativity. Because of its electron accepting nature, increasing number of nitro groups reduces electric density of the aromatic ring. On the other hand it is known that photocatalytic degradation is the oxidation by OH radical generated from the reaction between H_2O and positive hole [18,19]. Therefore it is understandable that aromatic compound substituted by more nitro groups is the less reactive with electrophilic OH radical. This effect of nitro group can be analyzed more quantitatively by the following Hammett law, as done for the

effect of chlorine substituent on the photocatalytic degradation of chlorophenol by Pichat et al. [17] in which another factor for the adsorption to TiO_2 is introduced.

$$\log k/k_o = \sigma\rho$$

where k and k_o are first-order rate constants of nitrophenolic compound and phenol, respectively, σ Hammett constant and ρ constant. σ of polynitrophenol was calculated as a sum of σ's of nitro groups, adopting the same values for ortho and para. The results are listed in Table 1. Neglecting the different adsorbability of each compound to TiO_2, good correlation was obtained between Hammett constant and apparent first-order rate constant. The contribution of the adsorbability to the degradation rate is apparently less in the case of nitrophenol than chlorophenol, because of larger σ value of nitrophenol.

Photocatalytic degradation of picric acid follows Langmuir–Hinshelwood equation. The rate constant and adsorption coefficient obtained by fitting our data to this equation are 7.1 μmol h^{-1} and 6.8 l mol^{-1}, respectively. As compared with the values for benzenesulfonate measured under the similar experimental condition [15], the rate constant is slower and adsorption coefficient is larger.

The addition of hydroxyl group to aromatic ring is a dominating reaction in the first part of the degradation, as discussed by many authors in the case of other aromatic compounds [16,17,20,21]. Fig. 9 indicates that the substitu-

Table 1
Apparent first-order rate constant of photocatalytic degradation of nitrophenolic compound and its Hammett constant [a]

	k_1 (min^{-1})	σ
4-NP	0.0072	0.78
2-NP	0.0072	0.78
3-NP	0.0067	0.71
2,4-DNP	0.0052	1.56
2,4,6-TNP	0.0033	2.34
PhOH	0.0155	0

[a] NP: nitrophenol, DNP: dinitrophenol, TNP: trinitrophenol, PhOH: phenol.

tion of nitro group and hydrogen atom on the aromatic ring by OH radical is the initial stage of photocatalytic reaction. Our results for the formation of aromatic intermediates can be explained by the combination of the effects of OH and nitro groups on armatic functionality. Ortho and para with regard to OH group is more negatively charged than meta, and hence more reactive with electrophilic OH radical, whereas meta with regard to nitro group is less positively charged and hence more reactive with OH radical than ortho and para. The formation of large amount of nitrohydroquinone from o-nitrophenol (Fig. 6) can be explained by the overlapping of the effects of OH and nitro groups. Fig. 6 shows that para with regard to OH group is more reactive with OH radical than ortho, and the effect of OH group is larger than that of nitro group. The former is also the case for 2,4-dinitrophenol (Fig. 6). Slower degradation of 3-nitrophenol than 4- and 2-nitrophenol (Fig. 1) can be also explained by the combination of the effects of OH and nitro groups: in 3-nitrophenol polarization is small due to cancelling of the adverse effects of OH and nitro groups, while in 4- and 2-nitrophenol ortho and para are negatively charged. The comparison between the amounts of intermediate compounds formed from phenol and nitrophenol indicated that hydrogen atom is replaced more easily than nitro group by OH radical as in the case of chlorophenol [22]. The same reactivity of OH radical was observed in the hydroxylation of 4-nitrophenol and 3-nitrophenol: the amount of hydroquinone formed from 4-nitrophenol is smaller than that of nitrohydroquinone from 3-nitrophenol (Fig. 6). This is in contrast with direct photolysis of nitrophenol in which nitro group increases the polarization of NO_2–C bond, and thus enhances the substitution of nitro group by OH group of water [23].

The formation of polyhydroxylated intermediate from 4-nitrophenol (Fig. 6) suggests that aromatic ring is substituted by OH radical consecutively. Fig. 4 indicated that the release of nitro group is one of the principal reactions in

the early part of the degradation of 4-nitrophenol. On the other hand the formation rates of NO_3^- from 2- and 3-nitrophenol and picric acid were slower (Fig. 9), suggesting that the substitution of hydrogen atom rather than nitro group by OH radical is more predominant at the initial stage of their photocatalytic degradations. The polyhydroxylation will subsequently lead to the opening of aromatic ring. However, considering the discrepancy between concentrations of denitrated aromatic compounds detected and that of NO_3^- formed (Figs. 6 and 9), there may be another pathway in which the opening of aromatic ring takes place before nitro group is substituted and nitrated aliphatic compound was formed [15,24].

Organic acids were formed as a result of the opening of aromatic ring. The formation of other highly hydrophilic compounds such as aldehyde, ketone and other carbonyl compounds can be expected as in the case of other oxidative degradation [14,15], although their identification was not attempted in this study. Among organic acids detected formic and acetic acids are largest in concentration. These two acids may be formed by the subsequent oxidation of other organic acids through the process proposed for the ozonation of phenol in our previous paper [25], in which the same organic acids were identified. When it is taken into consideration that formic acid is much more degradable than acetic acid, the formation of formic acid is much larger than that of acetic acid. Hence it can be considered that the large part of nitrophenolic compound eventually converted to CO_2 via formic acid.

Photocatalytic degradation of nitrogen-containing compound generates NO_3^-, NO_2^-, NH_4^+, N_2O and N_2 [26–29], according to the chemical structure surrounding nitrogen atom and experimental condition. From nitro group, NO_3^- is a major product and NH_4^+ is a minor one [6,26]. In our experiment the amounts of NO_3^- formed from 2×10^{-4} mol l^{-1} of 2,4-dinitrophenol and picric acid after 3 h are 80 and 70% of that of nitrogen contained in the respective compounds. Low et al. [26] reported that 2,4-dinitrophenol

Table 2
Ratio of NH_4^+ to NO_3^- formed from nitrophenolic compound at maximum formation [a]

NP compound	NH_4^+/NO_3^-
4-NP	0.33
3-NP	2.07
2-NP	1.85
2,4-DNP	0.25
2,4,6-TNP	0.20

[a] NP: nitrophenol, DNP: dinitrophenol, TNP: trinitrophenol.

forms NO_3^- and NH_4^+ by its photocatalytic degradation, and the ratio of NH_4^+ and NO_3^- is 0.12, and Minero et al. [6] reported 0.15 for nitrobenzene. In our experiment these ratios varied considerably with the compounds (Table 2). Nitro group on aromatic ring is considered to form NO_3^- when replaced by OH group. Since it is unlikely that NH_4^+ is formed by the reduction of NO_3^-, NH_4^+ may be formed by more complex procedure. This implies that some part of nitro group subsists after the opening of aromatic ring [24,25] as discussed earlier, and NH_4^+ is formed from nitrated aliphatic compound generated by the ring opening. In this respect it is to be noted that 2- and 3-nitrophenol in which nitro group is replaced from aromatic ring less easily than in 4-nitrophenol (Fig. 9), gave higher ratio of NH_4^+ to NO_3^-. It is also suggestive for slow formation of NO_3^- from picric acid at the early part of degradation that the photocatalytic degradation of 2,4,5-trichlorophenol is initiated by the direct reaction with positive hole, forming trichlorophenoxyl radical instead of the substitution of chlorine by OH radical [30].

5. Conclusion

The complete mineralization of mono-, di- and trinitrophenol was achieved by photocatalytic degradation. The degradation rate of nitrophenolic compounds decreases with an increasing number of nitro groups. Several polyhydroxylated aromatic intermediates were identified, which indicated the substitution of nitro group and hydrogen by OH radical. The substitution of nitro group of picric acid is less predominant than those of 4-nitrophenol and 2,4-nitrophenol at the early part of degradation. The ratio of NH_4^+ and NO_3^- formed by the degradation of nitrophenolic compound varied considerably with the compounds. In the mineralization process, the large part of CO_2 was considered to be formed via formic and acetic acids.

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