Photocatalytic hydroxylation of aromatic ring by using water as an oxidant

Hisao Yoshida,*[a] Hayato Yuzawa,[a] Masanori Aoki,[a] Kazuko Otake,[a]
Hideaki Itoh[b] and Tadashi Hattori[a]

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Electrophilic oxygen species photocatalytically derived from water molecules can selectively react with the aromatic ring of both benzene and its derivatives to produce the corresponding phenols and hydrogen over platinum-loaded titanium oxide when illuminated with light of appropriate wavelength in the absence of oxygen.

As we know, selective aromatic-ring oxidation of benzene derivatives such as alkylbenzenes is very difficult since the usual oxidants tend to react with the substituents first. In industrial processes for the production of phenols such as the cumene process,[1] benzene and alkylbenzenes are indirectly oxidized by using molecular oxygen at the expense of propene with acetone formation. Even in these cases, undesirable oxidation of side chains reduces the selectivity when we employ molecular oxygen as an oxidant. Thus, the development of novel selective oxidation systems has been desired from the viewpoint of green and sustainable chemistry.

Heterogeneous photocatalyses for the organic syntheses have received much attention because of their unique potential.[2] In recent decades, many studies on photocatalytic oxidation of both benzene and its derivatives have been carried out to yield corresponding phenols by using metal-loaded and unloaded TiO_2 photocatalyst,[3,4] mesoporous TiO_2,[5] TiO_2-pillared clay,[6] ion-exchanged zeolites[7] and so on. However, the selective aromatic-ring hydroxylation of benzene derivatives has not been reported. It is believed that some kinds of active oxygen species would be generated in these photocatalytic oxidation systems, such as superoxide, hydrogen peroxide and hydroxy radical,[8] which would not provide high selectivity. For the direct and selective oxidation of the aromatic ring, selective generation of electrophilic active oxygen species in the system would be important. In the present study, we thus examined photocatalytic oxidation of benzene and its derivatives by using water as an oxidant in the absence of molecular oxygen. We discovered a very interesting fact, namely that irradiation with light of selected wavelength provided highly selective hydroxylation of the aromatic ring.

Platinum-loaded titanium dioxide was prepared by a photodeposition method from TiO_2 (donated by the Catalysis Society of Japan as JRC-TIO-8, anatase, BET specific surface area: 338 m^2 g^{-1}, crystallites size estimated from X-ray diffraction: 7 nm) and $H_2PtCl_6\cdot 6H_2O$ (Kishida). The TiO_2 powder was dispersed into MeOH (50%) aqueous solution containing the Pt precursor in a Pyrex glass vessel with vigorous stirring, followed by photoirradiation from a 300 W Xe lamp, which emitted both UV and visible light, for 3 h with continuous stirring. The suspension was then filtered off with suction, washed with distilled water, and dried at 333 K. The samples are referred to as Pt(x)/TiO_2, where x is the Pt content (wt%) based on the weight of TiO_2. The Pt content was confirmed by ICP (inductively coupled plasma emission spectroscopy, Perkin-Elmer Optima 3300 DV). The diffuse reflectance UV–visible spectrum of the catalyst was recorded at room temperature on a JASCO V-570 equipped with an integrating sphere covered with $BaSO_4$. Before the photocatalytic reaction, the photocatalyst (0.2 g) in a quartz photoreactor (99 cm^3) was photoirradiated from beneath (18 cm^2) by the Xe lamp in air for 1 h to clean up the catalyst surface. After introducing substrate (1 ml) and distilled water (1 ml) in this order, the gas phase was purged with flowing Ar. Then, the mixture of substrate, water and the photocatalyst was magnetically stirred and photoirradiated from the Xe lamp under Ar atmosphere in the closed system at around room temperature for 3 h. In many cases in the present study, a band-pass filter was used between the reactor and the lamp to limit the irradiation light wavelength. After the photoreaction, first, the gas phase was collected with a syringe and analysed by GC–TCD. Then, methanol was added to the liquid phase and it was filtered. The filtrate was analysed by GC–MS and HPLC. In the present study, no reaction proceeded in the dark. In the absence of photocatalyst, no reaction occurred except for some photochemical reactions such as coupling. These results indicate that all the hydroxylation reactions observed in the present study proceed photocatalytically. In the presence of gaseous oxygen and photocatalyst, the degradation of substrates mainly occurred with low selectivity to phenols.

Table 1 shows the results for the photocatalytic reactions of benzene and alkylbenzenes with water in the absence of molecular oxygen. The TiO_2 without Pt loading was almost inactive for selective photooxidation of benzene though only small amounts of H_2 and CO_2 were observed (Entry 1). When Pt(0.1)/TiO_2 was employed without wavelength limitation of the irradiation light (Entry 2), phenol was obtained as the major organic product while other minor organic products such as biphenyl *via* coupling, cyclohexanol and cyclohexanone *via* consecutive hydrogenation of phenol, and large amounts of H_2 and CO_2†were also obtained. In the case of toluene, obtained products were cresol, bibenzyl and methylcyclohexanol with a larger amount of H_2,‡ and the cresol selectivity was quite low, such as 38% (Entry 4). When we selected the wavelength of the irradiation light by using a

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[a] *Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8603, Japan. E-mail: yoshidah@apchem.nagoya-u.ac.jp; Fax: +81-52-789-3178*
[b] *Division of Environmental Research, EcoTopia Science Institute, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8603, Japan*

Table 1 Photocatalytic oxidation of benzene and alkylbenzenes by TiO_2 and Pt/TiO_2 photocatalysts[a]

				Organic products/μmol				Gas products/μmol				
Entry	Substrate	Catalyst[b]	Irradiation light/nm	Phenols Y_{OH}	Coupling products[c] Y_C	Carbonyl products[d] Y_{CHO}	Hydrogenated compounds[e] Y_{HCP}	H_2	CO_2 Y_{CO2}	Total yield[f]/μmol Y	Conversion[g] (10^2%)	Phenols selectivity[h] (%) S_{OH}
1	Benzene	TiO_2	All[i]	n.d.	n.d.	—	n.d.	2.4	3.1	0.5	0.5	0
2		$Pt(0.1)/TiO_2$	All[i]	8.9	0.4	—	0.4	62	11	12	11	75
3		$Pt(0.1)/TiO_2$	405 ± 20[j]	3.7	0.4	—	0.5	9.4	n.d.	4.7	4.3	76
4	Toluene	$Pt(0.1)/TiO_2$	All[i]	11	7.8	0.3	0.5	240	11	29	32	38
5		$Pt(0.1)/TiO_2$	254 ± 20[j]	1.5	0.1	n.d.	n.d.	3.0	n.d.	1.7	1.9	88
6		$Pt(0.1)/TiO_2$	365 ± 20[j]	3.5	1.7	0.1	n.d.	31	n.d.	7.0	7.8	50
7		$Pt(0.1)/TiO_2$	405 ± 20[j]	5.7	1.4	0.1	n.d.	31	n.d.	6.6	7.3	86
8		$Pt(1)/TiO_2$	405 ± 20[j]	6.1	0.1	n.d.	n.d.	7.4	n.d.	6.3	7.0	97
9	Ethylbenzene	$Pt(1)/TiO_2$	405 ± 20[j]	3.4	0.3	n.d.	n.d.	6.0	n.d.	3.7	4.1	85
10	*tert*-Butylbenzene	$Pt(1)/TiO_2$	405 ± 20[j]	2.0	n.d.	n.d.	n.d.	6.3	n.d.	1.2	1.3	>99

[a] Catalyst: 0.2 g, reaction time: 3 h, H_2O: 1 ml, benzene: 1 ml (11 mmol) or alkylbenzene: 1 ml (9 mmol). The detection limits for organic products and CO_2 were 0.1 μmol and 1 μmol, respectively. [b] $Pt(x)/TiO_2$ contains x wt% of Pt. [c] Biphenyl for benzene, bibenzyl *etc.* for toluene, diphenylbutanes *etc.* for ethylbenzene. [d] Benzaldehyde for toluene. [e] Cyclohexanol and cyclohexanone for benzene, methylcyclohexanol for toluene. [f] $Y = Y_{OH} + Y_C \times 2 + Y_{CHO} + Y_{HCP} + Y_{CO_2}$/(number of carbons in a substrate molecule). [g] Calculated from the total yield. [h] S_{OH} (%) $= Y_{OH}/Y \times 100$. [i] No filter was used. Light intensity: 10 mW cm^{-2} (220–300 nm), 50 mW cm^{-2} (310–400 nm), 176 mW cm^{-2} (360–470 nm). [j] Band-pass filter was used. Intensity of the irradiation light, which could be absorbed by TiO_2, was 3 mW cm^{-2}. n.d. = not detected.

band-pass filter, it was found that the product selectivity varied with the wavelength. Fig. 1 depicts the effect of the irradiation light wavelength on the yield of cresol (the hydroxylation product) and the coupling products (the representative byproducts such as bibenzyl) in the reaction of toluene (*i.e.*, Table 1, Entries 5–7), where the absorption spectrum of the $Pt(0.1)/TiO_2$ photocatalyst is also shown. Since the intensity of the light that can be absorbed by TiO_2 (less than 400 nm) was adjusted to 3 mW cm^{-2} for each experiment, we can compare the product selectivity. It was found that the highest yield and selectivity of cresol were obtained when light around 385–425 nm was used. Since the main bandgap absorption of TiO_2 is less than around 380 nm and very small and broad bands are also found even around 400 nm, it is suggested that some kinds of photoexcitation other than the usual bandgap excitation are efficient for the selective hydroxylation. It is speculated that some surface defects such as hydroxyl groups or coordinatively unsaturated sites might function as photocatalytic active sites. Further investigation on the photoexcitation mechanism should be carried out. The platinum content also affected the selectivity. For the hydroxylation of toluene, the sample loaded with 1.0 wt% of platinum showed higher selectivity (97%) than the sample loaded with 0.1 wt% of platinum did (86%) (Entries 7 and 8), while for benzene hydroxylation the suitable platinum loading amount was lower than 1 wt%, typically around 0.1 wt%. In the optimum conditions with the moderate photocatalyst upon photoirradiation of selected wavelength around the absorption edge (405 ± 20 nm), the selectivity for the aromatic-ring hydroxylation of toluene was as high as 97%, where the production ratio of hydrogen to phenols was rather close to unity (Entry 8).§ In addition, aromatic-ring hydroxylation was also confirmed for ethylbenzene and *tert*-butylbenzene (Entries 9 and 10). These results suggest that the direct aromatic-ring hydroxylation with water occurs photocatalytically in these conditions, generally as shown in eqn (1).¶ Here, the water seems to act as an oxidant.

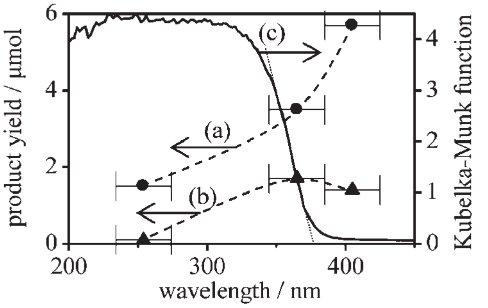
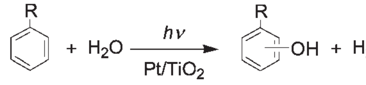


Fig. 1 Product yield of (a) cresol and (b) coupling products when illuminated with light of selected wavelength by using band-pass filters, and (c) a diffuse reflectance UV–visible absorption spectrum of $Pt(0.1)/TiO_2$. The permitted wavelength of light was 254 ± 20, 365 ± 20 and 405 ± 20 nm as indicated by horizontal bars. The intensity of the irradiation light, which can be absorbed by TiO_2, was 3 mW cm^{-2}.



(1)

Considering the product selectivity, the active oxygen species for the hydroxylation are suggested to be electrophilic. To confirm this and to establish the generality of this photocatalytic hydroxylation of the aromatic ring, various substituted benzenes were examined for this photocatalytic reaction. The yield and selectivity of the hydroxylated products are shown in Table 2 with the distribution of isomers, *i.e.*, *ortho*-, *meta*-, and *para*-directing substituted phenols. Corresponding phenols were obtained as the main products from every substrate listed here. The yield of hydroxylation products increased with increasing electron donating ability of the substituent from nitrobenzene to toluene (Table 2, Entries 1–6), except for anisole (Entry 7). The hydroxylation occurred

Table 2 Photocatalytic hydroxylation of various substituted benzenes[a]

		Hydroxylation products				
				Distribution of isomers (%)		
Entry	Substrate	Yield Y_{OH} (10^2%)[b]	Selectivity S_{OH} (%)[b]	*ortho-*	*meta-*	*para-*
1	Ph–NO_2	1.6	70	n.d.	>99	n.d.
2	Ph–CN	3.0	>99	n.d.	>99	n.d.
3	Ph–Cl	7.3	86	37	22	41
4	Ph–F	8.4	77	42	19	39
5	Ph–H[c]	8.8	77	—	—	—
6	Ph–CH_3	11	80	38	23	39
7	Ph–OCH_3	7.1	53	75	11	14

[a] Pt(0.1)/TiO_2: 0.2 g, H_2O: 1 ml, substrate: 1 ml (9.2–11 mmol), Irradiation light wavelength: 405 ± 20 nm, Light intensity: 5 mW cm^{-2} (measured at 310–400 nm), Reaction time: 3 h. [b] See the footnote of Table 1. [c] Benzene. n.d. = not detected.

only at the *meta*-position for the substrates having an electron-withdrawing group such as nitrobenzene and benzonitrile (Entries 1 and 2). On the other hand, the hydroxylation preferably occurred at the *ortho*- and *para*-position to some extent in the cases of the substrates having an electron-donating group such as chlorobenzene, fluorobenzene, toluene, and anisole (Entries 3–7). These results confirm that the reaction proceeds by a mechanism similar to that of electrophilic aromatic substitution and the active oxygen species in this photocatalytic reaction have an electrophilic character. For the substrates having a strongly electron-donating group such as phenol and aniline, the hydroxylation did not occur in the present conditions, while the side reactions preferably occurred through the activation of the electron-rich substituent. Anisole would give a lower yield of hydroxylation products for the same reason. These results were quite a contrast to the reported facts that, in an oxygen atmosphere on TiO_2 photocatalyst, nitorobenzene and benzonitrile did not show such a clear orientation effect, and phenol and aniline were hydroxylated clearly at *ortho*- and *para*-orientation before further oxidation.[3] Thus, the active oxygen species in the present conditions would be different from the major one in the presence of oxygen. It is also confirmed that the substituent effect could not follow the Hammett rule, suggesting that the reaction would be much influenced by the interaction between the substrate and the catalyst surface. From these facts, it is proposed that H_2O, OH^- or the surface hydroxy group of TiO_2 is oxidized by the photoformed hole on the surface to form an electrophilic oxygen species such as surface hydroxyl radical suitable for the photocatalytic hydroxylation, while molecular oxygen would be reduced by the photoexcited electron to form a nucleophilic oxygen species such as superoxide. In the absence of molecular oxygen, the active oxygen species would be limited to the electrophilic oxygen species derived from water and the aromatic-ring hydroxylation would proceed selectively.

To confirm the origin of the active oxygen species, labeled water containing 95.4% of $H_2{}^{18}O$ was employed in the reaction of toluene under light of the appropriate wavelength (405 ± 20 nm). As a result, 89% of the produced *ortho*-cresol contained the labeled oxygen atom ^{18}O. It is suggested that the water molecule acts as the main oxidant in the hydroxylation. At the same time, the participation of the oxygen from TiO_2, probably the surface hydroxy groups, is also suggested. Further investigation would be required to clarify the detailed reaction mechanism.

In conclusion, it was clarified that the direct aromatic-ring hydroxylation of benzene, alkylbenzenes and substituted benzenes could be promoted by platinum-loaded titanium oxide photocatalyst by using water as an oxidant in the absence of molecular oxygen. Photoexcitation with light of the appropriate wavelength slightly longer than the absorption edge, *i.e.*, above 380 nm, and the optimisation of the platinum loading amount were effective for improvement of the selectivity to produce phenols. It is suggested that the active oxygen species in this system are electrophilic ones derived from water and a photoformed hole, like hydroxy radicals, on the surface. The electrophilic active oxygen species would interact not with the substituents but with the electron-rich aromatic nucleus.

Notes and references

† Platinum is considered to reduce the recombination of photoexcited electrons and holes on TiO_2, and to accelerate the reduction of protons by the excited electron to produce hydrogen. H_2 and CO_2 would be formed as follows: $C_6H_6 + 12H_2O \rightarrow 6CO_2 + 15H_2$.

‡ In many cases, the amount of detected H_2 was much larger than the amount expected from the detected products, where other compounds that were undetectable in the present method might be formed to some extent.

§ The apparent quantum yield, roughly estimated from the number of the incident photons and the produced hydrogen, was *ca.* 0.8%.

¶ The reaction was confirmed to continue at least over 12 h and the photocatalyst was reusable: Even when the color of the photocatalyst became pale yellow due to the formation of byproducts from side reactions such as oligomerization, the photocatalyst could be refreshed by washing with benzene or toluene.

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