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# Photocatalysis of $H_3PW_{12}O_{40}$ for 4-Chlorophenol Decomposition in Aqueous Media[1)]

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Photocatalytic properties of $PW_{12}O_{40}{}^{3-}$ (abbreviated as $PW_{12}{}^{3-}$) for the 4-chlorophenol (4-CP) decomposition was investigated by using a 300 W Xe lamp at 35 °C in aqueous media. The rate of the 4-CP decomposition was not influenced by pH in the range from 1.0 to 2.0, where $PW_{12}{}^{3-}$ is stable. In the dark, no reaction proceeded. When the photolysis was carried out under $O_2$ atmosphere, 4-CP was decomposed and the catalyst remained in the oxidized form. In the deaerated solution, $PW_{12}{}^{3-}$ was reduced to $PW_{12}O_{40}{}^{4-}$ ($PW_{12}{}^{4-}$) by irradiation, the amount of $PW_{12}{}^{4-}$ formed during irradiation being approximately identical with the amount of 4-CP concurrently consumed. When the irradiation was stopped and $O_2$ was introduced, $PW_{12}{}^{4-}$ was oxidized rapidly to $PW_{12}{}^{3-}$ and a small amount of 4-CP decomposed.

Based on these facts we deduced that the reaction consists of the following three steps: (1) photoexcitation of $PW_{12}{}^{3-}$, (2) one-electron reduction of the excited $PW_{12}{}^{3-}$ to $PW_{12}{}^{4-}$ with simultaneous oxidation of 4-CP, and (3) reoxidation of $PW_{12}{}^{4-}$ to the original form by $O_2$. 4-CP is also decomposed in the last step, although the amount is much smaller than that in step (2). The dependency of the reaction rates on the concentration of substrate was explained by Langmuir (or Michaelis Menten) type kinetics, indicating that the complex formation between $PW_{12}{}^{3-}$ and 4-CP is the indispensable step of the photocatalytic decomposition.

Heteropoly compounds[2,3)] have both the acidity and the oxidizing ability, which can be systematically controlled by changing the constituent atoms and polyanion structures. Therefore, they are suitable materials for the catalyst design[4)] and they have been used in the homogeneous and heterogeneous catalytic systems.[5)] They are also effective photocatalysts and several groups have reported the photocatalytic oxidation of organic compounds by using heteropoly compounds.[6—8)]

A Keggin-type tungstophosphate, $PW_{12}O_{40}{}^{3-}$ (abbreviated by $PW_{12}{}^{3-}$), is a widely used photocatalyst, owing to the following characteristics. (1) It is readily synthesized and commercially available. (2) It is very soluble in water and its cluster size is approximately 1 nm, so that it may be regarded to be an easily accessible quantum-sized semiconductor. (4) The redox potential of photoexcited $PW_{12}{}^{3-}$ is 2.63 V (vs. NHE),[8)] so that it has potentially high oxidizing ability comparable to that of $TiO_2$. In fact, $PW_{12}{}^{3-}$ was quite effective for photocatalytic oxidation particularly in aqueous media.[9)]

It was reported that the order for the photocatalytic activity for alcohol dehydrogenation in water was $PW_{12}{}^{3-} > FeW_{12}O_{40}{}^{5-} > H_2W_{12}O_{40}{}^{6-}$.[9)] However, the order reversed in aqueous MeCN solution.[10)] Therefore, the high performance of $PW_{12}{}^{3-}$ in aqueous system cannot be accounted for only in terms of redox potential. In addition, the fundamental data such as pH effect on this system has not yet been clarified.

In the present study, as an extension of our on-going study on the catalytic properties of heteropoly compounds, we carried out the mechanistic and kinetic study on photocatalysis of $PW_{12}{}^{3-}$ in aqueous media as probed by the photodecomposition of 4-chlorophenol (abbreviated by 4-CP). We proposed in the present study on the basis of the results of reduction and oxidation of $PW_{12}{}^{3-}$ in the presence and absence of oxygen and irradiation that the photoactive species is the $PW_{12}{}^{3-}$ species and that the reaction proceeds via one-electron redox cycle. We further suggested the importance of pre-complexation for the catalytic activity. We chose this reaction because the reaction was well documented by Papaconstantinou et al.; according to their study, $PW_{12}{}^{3-}$ is the most effective among several polyoxometalates.[11)] In order to elucidate the factors controlling the catalytic activity, we focused on the early stage of the reaction. Considering the potential utilization of solar energy, we adopted a Xe lamp equipped with a cut filter which does not transmit the light in the wavelength $\lambda < 300$ nm.

## Experimental

**Materials.** Chlorophenols were purchased from Tokyo Kasei Co. and recrystallized twice in *n*-hexane before use. $H_3PW_{12}O_{40}$ was obtained from Nippon Inorganic Color & Chemical Co., Ltd. It was purified by ether extraction and recrystallized in water. Other reagents were used as received.

**Instrumentation.** High-pressure liquid chromatography (HPLC) was performed on a Shimadzu LC-9A using a absorbance detector equipped with a STR ODS-II reversed phase column. Gas chromatography (GC) was accomplished with a Shimadzu GC-8A equipped with a thermal conductivity detector and a Porapak Q column. Ultraviolet and visible absorption spectra (UV-vis) were obtained on a Shimadzu UV-2100 spectrophotometer. Nuclear magnetic resonance spectra were obtained on either a JEOL GX-400 or a JEOL EX-270 spectrometer.

Reaction solutions were irradiated with a 300W Xe lamp, usually with a UV-32 cut filter. All photoreactions were conducted in a cylindrical quartz cell (diameter 3.5 cm, cell length 3.0 cm).

**Photodegradation of Chlorophenols under Aerobic Conditions.** In a typical reaction, 10 ml of a 2.0 mM (1 M = 1 mol dm$^{-3}$) aqueous solution of chlorophenol was adjusted at pH = 1.0 with $HClO_4$. A cylindrical quartz vessel containing the reaction solution was then aerated by bubbling with $O_2$ and irradiated at 35 °C.

After photolysis, products in the liquid phase were determined on HPLC and NMR. Products in the gas phase were analyzed by means of GC-TCD.

In the pH effect experiments, the amount of $PW_{12}{}^{3-}$ in the reaction solution was calculated from the Lambert–Beer law. The absorption coefficient of $PW_{11}O_{39}{}^{7-}$ ($PW_{11}{}^{7-}$) was obtained from the UV-vis spectrum of the reaction solution at pH = 4.8, where the only polyanion present is $PW_{11}{}^{7-}$.

**Photoreaction under Anaerobic Conditions and Reoxidation under Aerated Conditions.** The reaction solution was prepared according to the same method as stated above. Prior to photoirradiation, the deaeration of the reaction solutions were carried out by vigorous bubbling with Ar for more than 5 min. Production of heteropolyblue was quantified by means of the UV-vis spectroscopy following the change of the Inter-Valence Charge Transfer absorption band as reported earlier.[12] Fairly good reproducibility was obtained.

After the above reaction, $O_2$ was introduced slowly into the resulting solution. After 1 h, when the catalyst was completely reoxidized, the solution was analyzed by HPLC. The reaction was usually repeated several times in order to assure the reproducibility.

## Results

**Reaction under the Aerobic Conditions.** $PW_{12}{}^{3-}$ is quite stable at pH 1.0 in water. The stability of the catalyst against photolysis ($\lambda$ > 300 nm) was confirmed by UV-vis spectroscopy prior to the reaction. In the dark, no reaction took place at least for several months. When the absorption edge of the ligand to metal charge transfer (LMCT) band was irradiated, 4-CP was decomposed. An example of the time course of the photodegradation of 4-CP is shown in Fig. 1. The catalyst concentration was optimized to be 0.7 mM (see below). With purified 4-CP, the reaction followed pseudo-first order kinetics. The color of the reaction solution remained colorless and pH was unchanged during the irradiation. 4-CP was completely consumed within several hours. When the reaction was carried out without purification of 4-CP, the time profile became much different, showing an induction period. This indicates that organic impurity affects the reaction rate. One of the main products in the solution was hydroquinone, which increased with a decrease in the substrate. The trace amount of phenol was produced in the present system. A little lower rate was observed as compared to the Papaconstantinou's results;[11] this is ascribed to the lower power of the lamp used in the present study.

When the photolysis was carried out without the catalyst, 4-CP was decomposed to a small extent (Fig. 1). The amount of 4-CP consumed after 2 h irradiation was not dependent on pH in the range of pH 1.0—7.0. In this case, the main product was benzoquinone.

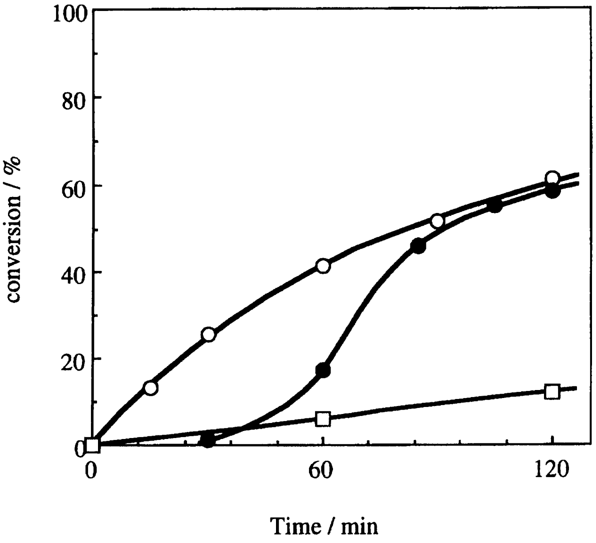

Fig. 1. Time courses for photocatalytic decomposition of 4-chlorophenol with $H_3PW_{12}O_{40}$ under $O_2$ saturated conditions, $[PW_{12}]$=0.7 mM; [4-CP]=2.0 mM; pH=1.0, $\lambda$ >320 nm. ○, run with purified 4-CP; and □, photolysis without catalyst; ●, with non-purified 4-CP.

**pH Effect on the Catalytic Activity.** When the UV-vis spectra of $PW_{12}{}^{3-}$ in aqueous solution ($\lambda_{max}$; 265 nm) were measured, the oxygen-to-metal charge-transfer transition band did not change in the pH range 1.0—2.0. Without the addition of $HClO_4$, pH was 2.5 and 26.8% of $PW_{12}{}^{3-}$ was transformed to $PW_{11}O_{39}{}^{7-}$ ($PW_{11}{}^{7-}$) (Fig. 2). Dependence of the catalytic activity on pH is shown in Fig. 3. When the photodegradation of 4-CP was carried out in the pH range of 1.0—2.0, the catalytic activity was approximately constant, but the reaction rate sharply decreased above about pH 2.5.

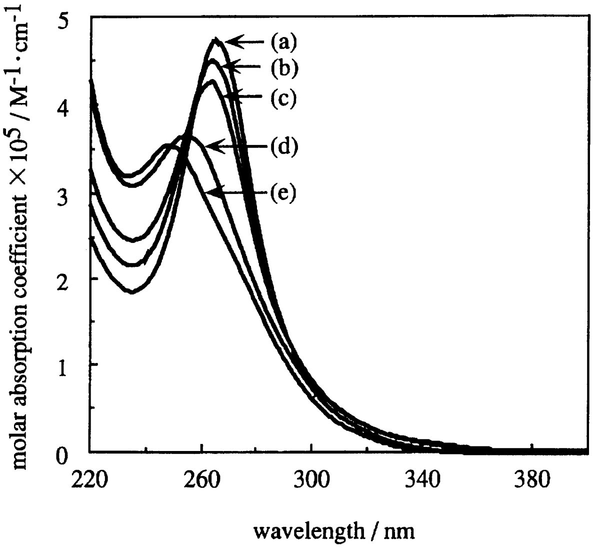

Fig. 2. UV-vis spectrum of $PW_{12}{}^{3-}$ in aqueous solution. (a) pH = 1.0—2.0, (b) 2.5, (c) 2.7, (d) 3.7, and (e) 4.80. pH was adjusted with $HClO_4$.

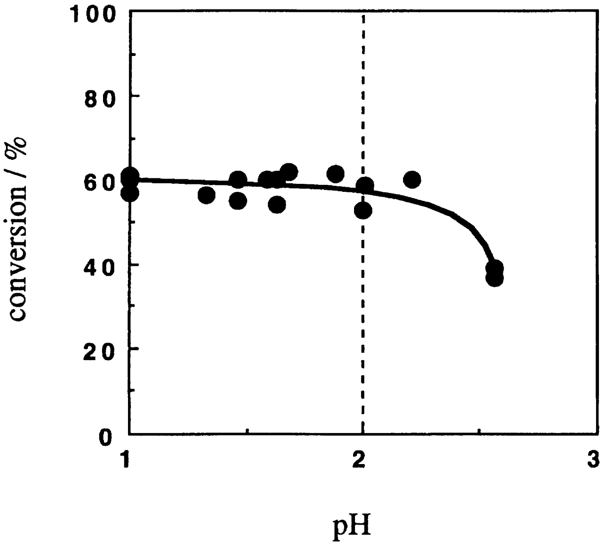

Fig. 3. Dependence of the initial rate of 4-chlorophenol photodecomposition by $PW_{12}^{3-}$ on pH. $[PW_{12}] = 0.7$ mM; $[4\text{-CP}] = 2.0$ mM; pH was adjusted with $HClO_4$.

**Reaction under Anaerobic Conditions.** Irradiation of the reaction solution which was adjusted at pH 1.0 resulted in the color change to blue in the absence of air and strong inter-valence charge-transfer (IVCT) absorption band ($\lambda_{max}$ : 498 nm, $\lambda_{max}$ : 750 nm)[7] appeared in the visible region (Fig. 4), indicating the formation of heteropolyblue, the reduced form of the catalyst. In contrast to the alcohol dehydrogenation systems in which $PW_{12}O_{40}^{5-}$, a two-electron reduced polyanion, was formed in addition to one-electron reduced $PW_{12}^{4-}$,[13—15] only $PW_{12}^{4-}$ was formed in this system as reported in the literature.[11] As shown in Fig. 5, 4-CP decomposed in this photoreduction process and the amount of 4-CP consumed was comparable with the amount of the heteropolyblue formed. Thus, the reduction of one mole of heteropolyanion is accompanied by the decomposition of approximately one mole of 4-CP. The main products under anaerobic conditions were the same as those under aerobic conditions. When the reaction solution in the absence of 4-CP was irradiated, $PW_{12}^{3-}$ was also reduced, although the reduction rate was much smaller that in the presence of 4-CP (Fig. 5).

After 2 h, the irradiation of the reaction solution containing $PW_{12}^{4-}$ and 4-CP was stopped and the solution was exposed to the air. Results are also shown in Fig. 5. The characteristic blue color gradually faded, concomitantly with both the disappearance of the IVCT bands and the recovery of the absorbance in the LMCT band. This indicates the transformation of the reduced $PW_{12}^{4-}$ to the original form, $PW_{12}^{3-}$. In this step, 4-CP was further consumed, although the amount was small. The rate of this reoxidation step is dependent on the method of $O_2$ introduction. For instance, when $O_2$ was bubbled into the reaction solution containing $PW_{12}^{4-}$, the heteropolyblue was very rapidly reoxidized to $PW_{12}^{3-}$, indicating that the dissolution and diffusion of $O_2$ is rate-limiting. Nevertheless, the amount of 4-CP consumed in the reoxidation step did not appreciably depend on the way of $O_2$ introduction to the solution. In this step, a small amount of hydroquinone was produced.

**Kinetic Study.** The dependence of the reaction rate on the catalyst concentration is shown in Fig. 6. The rate was proportional to the catalyst concentration in the optically dilute region. At the catalyst concentration higher than 0.7 mM, the rate was saturated due to complete light absorption by catalyst.

The effects of the concentration of 4-CP on the reaction rates are shown in Fig. 7. The rates show saturation at high

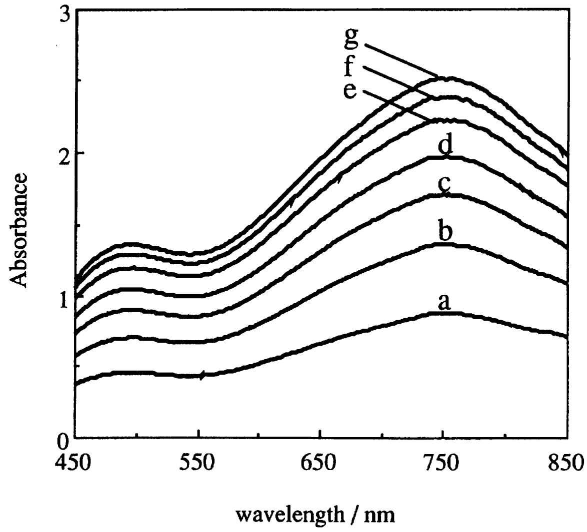

Fig. 4. Time dependence of the production of the reduced $\alpha$-$PW_{12}O_{40}^{4-}$ chromophore upon irradiation of the reaction solution at 15 min intervals under deaerated conditions. $[PW_{12}^{3-}]=0.7$ mM, $[4\text{-CP}]=2.0$ mM, cell length$=3.0$ cm. (a) After 15, (b) 30, (c) 45, (d) 60, (e) 75, (f) 90, and (g) 105 min.

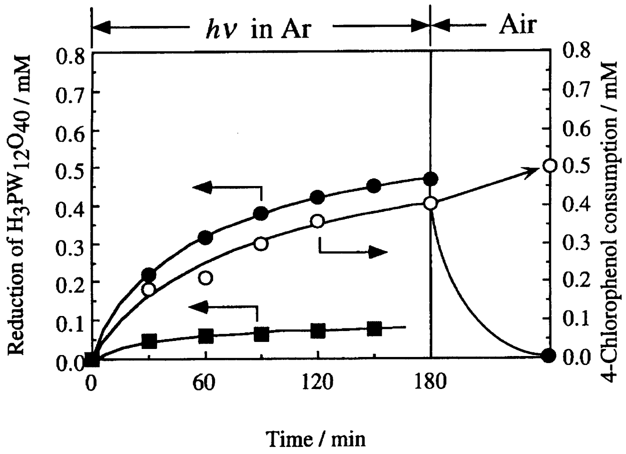

Fig. 5. Time course for photocatalytic decomposition of 4-chlorophenol with $H_3PW_{12}O_{40}$ under deaerated conditions. $[PW_{12}]=0.7$ mM; $[4\text{-CP}]=2.0$ mM; pH$=1.0$, $\lambda > 320$ nm. ●, the amount of reduced $PW_{12}O_{40}^{3-}$; ○, the amount of 4-chlorophenol consumed; ■, reduction of $PW_{12}^{3-}$ in the absence of substrate. At the vertical line in the figure, the irradiation was stopped and air was introduced (see text).

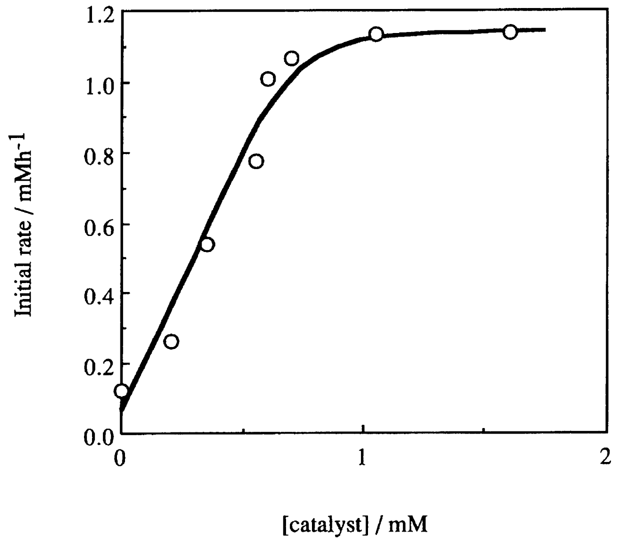

Fig. 6. Dependence of the catalytic activity for 4-chlorophenol photodecomposition by $PW_{12}{}^{3-}$ on the catalyst concentration. [4-CP] = 2.0 mM; pH was adjusted at 1.0 with $HClO_4$.

concentration of the substrate. The saturated value increased with the catalyst concentration, indicating Langmuir type (or Michaelis–Menten type) kinetics. As discussed in a later section, the reciprocal plot according to the Langmuir-type kinetics shows a linear correlation (Fig. 8).

**Effect of Alcohol on the Catalytic Activity.** The effect of the addition of organic impurity is shown in Table 1. The presence of a small amount of ethanol retarded the reaction, and the effect increased with an increase in the amount of ethanol added. Similar results were observed for other alcohols such as 2-propanol.

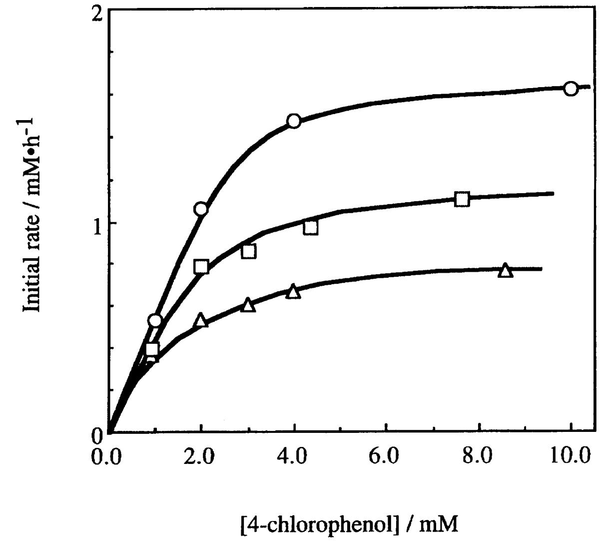

Fig. 7. Dependence of the initial rate of 4-chlorophenol photodecomposition by $PW_{12}{}^{3-}$ on 4-chlorophenol concentration. ○, $[PW_{12}]$ = 0.7 mM, □, 0.5 mM, △, 0.35 mM; pH was adjusted at 1.0 with $HClO_4$.

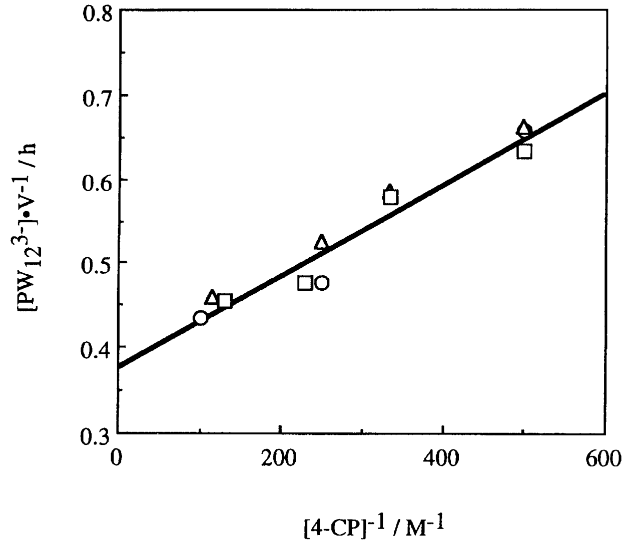

Fig. 8. Plot of 1/rate (M s$^{-1}$) versus 1/[4-CP]. The symbols refer the same as in Fig. 7.

Table 1. Effect of Ethanol Addition on Photodecomposition of 4-Chlorophenol under Aerobic Conditions ($\lambda$ > 320 nm)

| Amount of ehtanol added (mM) | Conv. (%) |
|---|---|
| 0.00 | 61 |
| 2.00 | 45 |
| 10.00 | 30 |

Irradiation time 2 h; reaction temperature 35 °C; $[H_3PW_{12}O_{40}]$ = 0.7 mM; [4-CP] = 2.0 mM; 300 W Xe lamp; pH was adjusted at 1.0 with $HClO_4$.

**Photodegradation of Other Chlorophenols.** The catalytic activities of $PW_{12}{}^{3-}$ for several chlorophenols are shown in Table 2. $PW_{12}{}^{3-}$ was also effective for polychlorophenols. The reactivity increased with the extent of chlorine substitution, phenol being least reactive.

## Discussion

**Comparison with Earlier Results.** When the absorption band of 4-CP is irradiated in aqueous solution, 4-CP is decomposed, as reported in the literature.[16)]

Table 2. Photocatalytic Decomposition of Chlorinated Phenols with $H_3PW_{12}O_{40}$ ($\lambda$ > 320 nm) under Aerated Conditions

| Substrate | Conversion<br>mol% |
|---|---|
| Phenol | 35 |
| 4-Chlorophenol | 61 |
| 2, 4-Dichlorophenol | 64 |
| 2, 4, 6-Trichlorophenol | 75 |

Irradiation time in all cases 2 h; [catalyst] = 0.7 mM; [substrate] = 2.0 mM; reaction temperature 35 °C; source 300 W Xe lamp; pH was adjusted at 1.0 with $HClO_4$.

$$4\text{-CP} + h\nu \rightarrow 4\text{-CP}^* \xrightarrow{O_2} \text{benzoquinone}. \tag{1}$$

4-CP does not show absorption in the range $\lambda > 320$ nm. However, when the irradiation was carried out with a UV-32 cut filter in the absence of $PW_{12}{}^{3-}$, 4-CP was decomposed to some extent as shown in Fig. 1. This is due to the property of the cut filter which slightly transmits light in the shorter wavelength. The use of another cut filter having lower transmission below 320 nm significantly suppressed the decomposition of 4-CP. The photodecomposition observed in the present work in the absence of $PW_{12}{}^{3-}$ very probably proceeds via reaction (1) because the main product was benzoquinone.

**pH Effect on Catalytic Activity.** The stability of $PW_{12}{}^{3-}$ in aqueous solution is strongly dependent on pH.[2,17] It is quite stable at pH ca. 1.0. At pH 1.5—2.0, it is rapidly (and reversibly) converted to lacunary $PW_{11}{}^{7-}$ anion according to Eq. 2.[2]

$$PW_{12}O_{40}{}^{3-} + (5-x)OH^- \rightleftharpoons H_xPW_{11}O_{39}{}^{(7-x)-} + HWO_4^- + (2-x)H_2O \tag{2}$$

However, the invariancy of the UV-vis spectra at pH 1.0—2.0 (Fig. 2 spectra a—e) indicates that the dominant species in this range was $PW_{12}{}^{3-}$. Accordingly, as shown in Fig. 2, the catalytic activity did not change in this range. On the other hand, the catalytic activity decreased above pH=2.0, corresponding to the change of the absorbance of the LMCT band. Thus, the catalytically active species is very probably $PW_{12}{}^{3-}$.

The constant catalytic activity in the pH range 1.0—2.0 implies that the activity is not dependent on the ionic strength. This was confirmed by the fact that the addition of other electrolytes such as KCl had no influence on the activity.

**Reaction Mechanism.** Photooxidation of organic compounds such as alcohols and alkanes catalyzed by heteropolyacids in aerated and deaerated solution is generally described by the following steps.

$$\text{POM} + h\nu \rightarrow \text{POM}^* \tag{3}$$

$$\text{POM}^* + \text{SubH}_2 \rightarrow \text{POMred} + \text{Sub}_{\text{ox}} + 2\text{H}^+ \tag{4}$$

$$\text{POMred} + 2\text{H}^+ + \text{O}_2 \rightarrow \text{POM} + \text{H}_2\text{O (aerated solution)} \tag{5}$$

$$\text{POMred} + 2\text{H}^+ \rightarrow \text{POM} + \text{H}_2 \text{ (deaerated solution)} \tag{6}$$

Here, POM, POM*, $SubH_2$, POMred, and $Sub_{ox}$ refer to polyoxometalates, photoexcited polyoxometalates, organic substrate, reduced POM, and oxidized form of organic substrate, respectively. The reaction consists of photoreduction steps ((3) and (4)) and a reoxidation step ((5) or (6)). In the presence of $O_2$, $PW_{12}{}^{3-}$ can probably accept only one electron, since the reoxidation is so fast that the reduced species $PW_{12}{}^{4-}$ cannot be susceptible to further reduction.[7] Under the aerated conditions, the degree of the reduction depends on the substrate. For instance, $PW_{12}{}^{5-}$, the two-electron reduced species, can be produced when alcohols are the substrates,[13—15] while it is not formed when alkanes are the substrates.[18,20] In the present system where 4-CP is the substrate, only $PW_{12}{}^{4-}$ is the reduced species, as reported earlier.[11]

In the absence of $O_2$, the reoxidation step is very slow as compared to the photoreduction step. Therefore, the irradiation under the deaerated conditions would provide information on the photoreduction step. By the irradiation in the absence of 4-CP under deaerated conditions, $PW_{12}{}^{4-}$ was slightly accumulated. This is explained by the oxidation of water, as described in step (7). Yamase et al. observed the formation of OH• by the irradiation of isopolyanions in water.[19] The reduced heteropolyanion may be reoxidized by Eq. 8.[20]

$$PW_{12}{}^{3-*} + H_2O \rightarrow PW_{12}{}^{4-} + OH\cdot + H^+, \tag{7}$$

$$PW_{12}{}^{4-} + OH\cdot + H^+ \rightarrow PW_{12}{}^{3-} + H_2O. \tag{8}$$

In the presence of 4-CP under deaerated conditions, the rate of photoreduction of $PW_{12}{}^{3-}$ to $PW_{12}{}^{4-}$ was greatly enhanced as compared with that in the absence of 4-CP. Since the amount of 4-CP which decomposed during irradiation was comparable with the amount of $PW_{12}{}^{3-}$ reduced, the enhanced photoreduction step is due to step (9). In the presence of 4-CP, the OH• radical produced by eq. (7) may be consumed by Eq. 10.

$$PW_{12}{}^{3-*} + 4\text{-CP} \rightarrow PW_{12}{}^{4-} + 4\text{-CP}_{\text{ox}}{}^+ \tag{9}$$

$$OH\cdot + 4\text{-CP} \rightarrow \text{addition and/or Cl}\cdot \text{ abstraction.} \tag{10}$$

Here $4\text{-CP}_{ox}{}^+$ refers to oxidized forms of 4-CP.

The result that the amount of 4-CP consumed is approximately equal to the amount of $PW_{12}{}^{4-}$ formed in the initial stage of the reaction also indicates that the radical chain reaction is negligible. This is supported by the fact that few products expected for radical chain reaction such as phenol were detected.

The reoxidation of $PW_{12}{}^{4-}$ by $O_2$ can be described as follows:[21]

$$PW_{12}{}^{4-} + O_2 \rightarrow PW_{12}{}^{3-} + O_2{}^-. \tag{11}$$

The consumption of 4-CP observed when $O_2$ was introduced into the reaction system after 2 h irradiation (Fig. 5) indicated the formation of active oxygen species in the reoxidation step. However, the amount of 4-CP consumed was much smaller, so that the decomposition in the photoreduction step is the major path for 4-CP decomposition. The fate of $O_2{}^-$ is not elucidated, but OH• may be produced,[22] as indicated by the formation of hydroquinone.

In contrast to the photoreaction under deaerated conditions, heteropolyblue was not observed at all in the presence of $O_2$. This means that the reoxidation step is much faster than the photoreduction step. Hence, the rate-determining step is presumed to be the photoreduction step.

It has been reported for illuminated $TiO_2$ systems that the rate of the decomposition of 4-CP obeys Langmuir kinetics.[23] This is also the case with the present system. A reaction mechanism consistent with the present experimental data is given in Eqs. 11, 12, 13, 14, 15, and 16. If the steady-state approximation is applied to the concentration of the excited state of complex (step (13)) for a constant light intensity and the small contribution of the 4-CP decomposition in the reoxidation step is neglected, the rate of the 4-CP decomposition, $V$, can be described by Eq. 16.

$$\mathrm{PW_{12}}^{3-} + \text{4-CP} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{PW_{12}}^{3-}\cdots\text{4-CP} \tag{12}$$

$$\mathrm{PW_{12}}^{3-}\cdots\text{4-CP} + h\nu \xrightarrow{k_2} \mathrm{PW_{12}}^{3-*}\cdots\text{4-CP} \tag{13}$$

$$\mathrm{PW_{12}}^{3-*}\cdots\text{4-CP} \xrightarrow{k_{\mathrm{ic}}} \mathrm{PW_{12}}^{3-}\cdots\text{4-CP} \tag{14}$$

$$\mathrm{PW_{12}}^{3-*}\cdots\text{4-CP} \xrightarrow{k_3} \mathrm{PW_{12}}^{4-} + \text{hydroquinone, etc} \tag{15}$$

$$\mathrm{PW_{12}}^{4-} + \mathrm{O_2} \xrightarrow{\text{fast}} \mathrm{PW_{12}}^{3-} + \mathrm{O_2^-} \tag{11}$$

$$V = k'K[\mathrm{PW_{12}}^{3-}]_0 \cdot [\text{4-CP}]_0/(K[\text{4-CP}]_0 + 1) \tag{16}$$

$$K = k_1/k_{-1}$$

$$k' = k_2k_3/(k_3 + k_{\mathrm{ic}}).$$

Here $[\mathrm{PW_{12}}^{3-}]_0$ and [4-CP] are the initial concentration of the catalyst and 4-CP, respectively.

From the reciprocal plots between the 4-CP concentration and the initial rate for 4-CP decomposition, as shown in Fig. 8, numerical values were obtained for $k'$ and $K$: 2.64 $\mathrm{h}^{-1}$ and $6.9\times10^2$ $\mathrm{M}^{-1}$. By using these values, the rates are calculated; they are compared with the experimental data in Fig. 9. A good agreement between the two supports the above kinetics. According to the value of $K$, 60% of the catalyst ligate to 4-CP under the standard conditions ($[\mathrm{PW_{12}}^{3-}]_0$=0.7 mM, $[4-\mathrm{CP}]_0$=2.0 mM).

These considerations indicate that there are two factors controlling the catalytic activity for photoreaction with polyoxometalats: (i) the complexation between the catalyst and the substrate, and (ii) the reactivity of the substrate with the photoexcited catalyst. The effects of chlorine substitution on the photodecomposition of chlorophenols, shown in Table 2, may be brought about through these two factors.

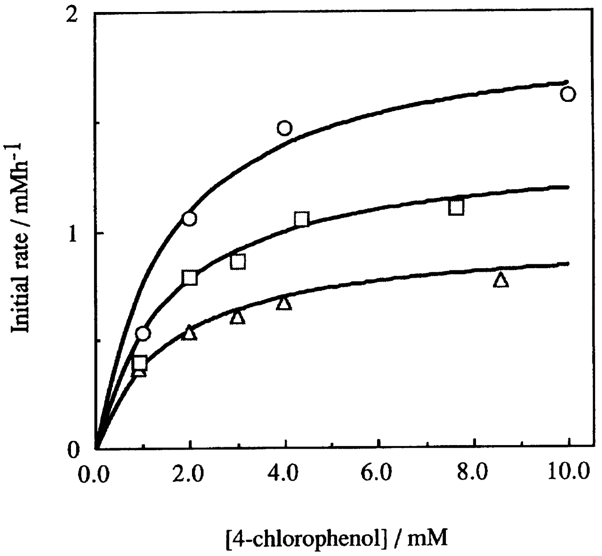

Fig. 9. Comparison between experimental data and calculated values. The symbols refer the same as in Fig. 7.

There are various pieces of spectroscopic evidence for the presence of the significant interaction between heteropolyanion and organic compounds. Pope et al. investigated the basicity of the Keggin-type polyanion by NMR of hydrated chloral.[24] Fox et al. reported by means of NMR and fluorescence lifetime measurement that $\mathrm{PW_{12}}^{3-}$ coordinates with alcohols.[10] By means of X-ray structural characterization, Hill et al. showed that there was unambiguous interaction between tetramethylurea (TMU) and $H_3PMo_{12}O_{40}$.[25] In the present work the strong interaction was kinetically demonstrated and we were able to evaluate the interaction quantitatively and directly in the catalytic system.

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