Photocatalyzed Decomposition of 4-Chlorophenol by Keggin-Type Heteropolytungstate[#]

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The photocatalytic decomposition of 4-chlorophenol with a Keggin-type heteropolytungstate, $PW_{12}O_{40}{}^{3-}$ (abbreviated as $PW_{12}{}^{3-}$), under aerated conditions has been investigated in an aqueous or water-acetonitrile solution by using a 300 W Xe arc lamp at 303 K. The kinetics of the reaction indicated that the reaction proceeds via a Langmuir–Hinshelwood (or Michaelis–Menten) type mechanism, in which the complexation between the heteropolyanion and 4-chlorophenol exists as a pre-equilibrium step. This complex formation was evidenced by the observation of a new band at $\lambda < 650$ nm and the enhancement of the solubility of 4-chlorophenol in water in the presence of $PW_{12}{}^{3-}$. The intensity of the new band varied in parallel with the reaction rate, depending on the concentrations of 4-chlorophenol and acetonitrile. This fact was consistent with the mechanism proposed.

Heteropoly compounds have been used for various reactions in both homogeneous and heterogeneous systems.[1,2] They are also effective photocatalysts for the oxidation of alcohols,[3] alkanes,[4] and amines.[5]

Recently, Papaconstantinou et al. reported that the photoactivated polyoxometalates efficiently decomposed chlorophenols to CO_2 and HCl,[6,7] and that $PW_{12}O_{40}{}^{3-}$ (abbreviated as $PW_{12}{}^{3-}$) was more effective than TiO_2. Hence, $PW_{12}{}^{3-}$ is potentially a promising photocatalyst for the treatment of waste water. The photochemical properties of $PW_{12}{}^{3-}$ have extensively been investigated.[8] However, the factors controlling the catalytic activity are not elucidated and the reaction mechanism of the photodecomposition of chlorophenols remains unclarified, while the alcohol photooxidation has been well documented by several groups.[3d,3f,9]

Previous reports showed that the photodecomposition of 4-chlorophenol catalyzed by $PW_{12}{}^{3-}$ consists of the photoreduction and reoxidation steps.[7,10] We previously suggested on the basis of the kinetic study that the reaction proceeds via a Langmuir–Hinshelwood (or Michaelis–Menten) type mechanism and that the precomplexation between polyanion and substrate is an important factor controlling the catalytic activity.[10]

In this study, extending the previous work, we attempted to provide evidence for the presence of precomplexation between the heteropolyanion and 4-chlorophenol, and further to demonstrate the importance of the complexation in photocatalysis. Therefore, we focused on the initial stage of the photoreaction. Here we mainly used a Xe lamp with a 340 nm cut-off filter in order to avoid the direct photolysis, whereas a 320 nm cut-off filter was used in the previous study.[10]

Experimental

Materials. 4-Chlorophenol was purchased from Nacalai Tesque and Tokyo Kasei Co. It was recrystallized twice in hexane prior to use. Keggin-type heteropolytungstate, $H_3PW_{12}O_{40}$, was obtained from Nippon Inorganic Colour & Co., Ltd. It was purified by ether extraction and recrystallized from water to exclude the ether, since even a trace amount of organic impurity affects the reaction rates.[10] ^{31}P NMR in aqueous solution confirmed the absence of lacunary polyanions. Acetonitrile (analytical grade) was purchased from Nacalai Tesque and used without further purification.

Analysis. High-performance liquid chromatography (HPLC) was carried out on a Shimadzu LC-9A equipped with a UV detector and an STR ODS-II reversed phase column. Ultraviolet and visible absorption spectra were recorded on a Shimadzu UV-2100 spectrophotometer and NMR spectra on either a JEOL GX-400 or a JEOL EX-270 spectrometer.

Photoreaction. Reaction solution were irradiated with a Cermax 300 W-Xe lamp, equipped with a cut-off filter. In order to avoid overheating, a reflecting filter (Kenko Co. Ltd.) which reflects the light and transmits the heat was used. All photoreactions were conducted in a cylindrical quartz cell (diameter, 3.5 cm and path length, 3.0 cm).

The photoreaction under aerated conditions or deaerated conditions was carried out at 303 K as in the previous work.[10] The identification and quantification of the organic compounds in the solution were made by HPLC and ^{1}H NMR.

Photoreduction of $PW_{12}O_{40}{}^{3-}$ under Deaerated Solution. In a typical run, the reaction solution was bubbled with Ar for more than 5 min and then irradiated by the Xe lamp with the 360 nm cut filter. This bubbling was previously shown sufficient to saturate oxygen in the solution.[10] Small portions of the sample solution were withdrawn at regular intervals, and quickly measured on a UV-vis spectrometer. The resulted heteropolyblue was quantified using the molar absorption coefficient of the characteristic intervalence charge transfer band of $PW_{12}{}^{4-}$.[11] Although the spectro-

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[#] Catalysis by Heteropoly Compounds. Part. 33.

scopic measurement was carried out in air, the reoxidation of the reduced polyanion was negligible during the manipulation and good reproducibility was obtained.

Measurement of the Solubility of 4-Chlorophenol in Water. To an aqueous solution containing PW_{12}^{3-} which was kept at 295 K, an appropriate amount of 4-chlorophenol was added, and then the UV-vis spectrum of the solution was recorded. The absorbance of the new absorption band which appears in the visible region increases with an increase in the concentration of 4-chlorophenol (vide infra), as long as the solution is homogeneous. The total amount of 4-chlorophenol added until the absorbance of the new band stopped increasing was regarded as the solubility of 4-chlorophenol.

Results

Photocatalytic Decomposition of 4-Chlorophenol with PW_{12}^{3-}. The UV-vis spectrum of $H_3PW_{12}O_{40}$ (abbreviated as PW_{12}^{3-}) in the aqueous solution and the characteristic transmittance of the cut-off filters are shown in Fig. 1. PW_{12}^{3-} showed a peak ($\lambda_{max} = 265$ nm) as in the literature.(11) The 320 nm filter and 340 nm filter do not transmit the light of the wavelengths $\lambda < 300$ nm and $\lambda < 320$ nm, respectively.

The results of the photocatalytic decomposition of 4-chlorophenol with PW_{12}^{3-} under the diluted conditions ([catalyst] = 0.7 mM, [4-chlorophenol] = 2.0 mM, 1 M = 1 mol dm^{-3}) in the O_2 saturated solutions are summarized in Table 1. General behavior of the catalysts with a 340 nm cut-off filter was essentially the same as in that of the previous work(10) where 320 nm filter was used, although the direct photolysis of 4-chlorophenol in the absence of catalyst did not occur with the 340 nm cut-off filter. Therefore, we adopted the 340 nm cut-off filter in the present study. The data in the last line in Table 1 show that, when the photoreaction was carried out in the 50% acetonitrile-50% water solution, the reaction rates were very much suppressed.

Table 1. Photocatalytic Decomposition of 4-Chlorophenol with Phosphododecatungstate under Aerated Conditions[a)]

Cut-off filter	Solvent	Conversion/%	
		With catalyst	Without catalyst
UV-32	H_2O[b)]	61	12
UV-34	H_2O[b)]	60	< 1
UV-34	50% MeCN/50% H_2O	< 1	< 1

a) Irradiation time; 2 h, source; 300-W Xe arc lamp with cut-off filters (see Experimental Section). Reactions were carried out in 10 ml of water in a cylindrical quartz vessel. [catalyst] = 0.7 mmol L^{-1}; [4-chlorophenol] = 2.0 mmol L^{-1}; b) pH was adjusted at 1.0 with $HClO_4$.

Kinetics of the 4-Chlorophenol Photodecomposition. Figure 2 shows the dependence of the initial rate of the photodecomposition of 4-chlorophenol (4-CP) on the 4-chlorophenol concentration ($\lambda > 340$ nm). The reaction rate was saturated at high concentrations of the substrate. Similar behavior has previously been reported using 320 nm cut-off filter.(10) The reciprocal plot shows a linear correlation, as shown in Fig. 3.

Subsequently, the effect of the addition of acetonitrile on the rate of 4-chlorophenol photooxidation was investigated. For each concentration of 4-chlorophenol (1.0, 2.0 mmol L^{-1}), the reaction rate decreased with an increase in the concentration of acetonitrile. The plot of the reciprocal of the reaction rate vs. the concentration of acetonitrile is shown in Fig. 4. Linear correlations are observed.

UV-vis Spectra of the Reaction Solutions. When 4-chlorophenol was added into the aqueous solution containing PW_{12}^{3-}, a new absorption band appeared in the visible

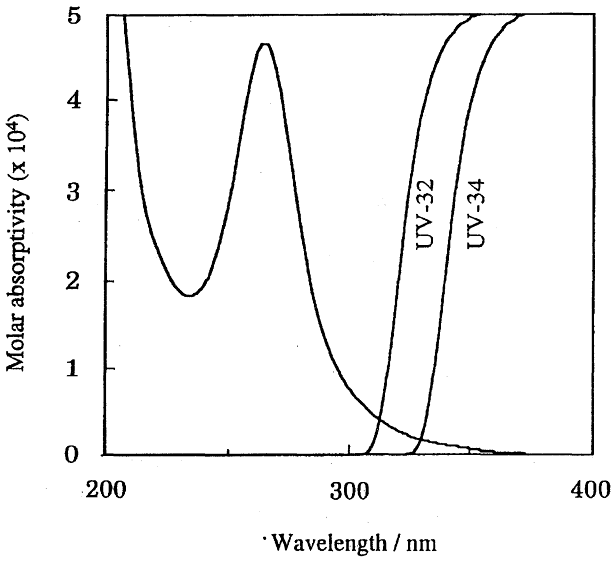

Fig. 1. UV-vis absorption spectrum of $H_3PW_{12}O_{40}$ in aqueous solution and the transmission characteristics of the cut-off filters UV-32 and UV-34. [$H_3PW_{12}O_{40}$] = 0.5 mM. pH was adjusted at 1.0 and a cell with 1 mm path length was used.

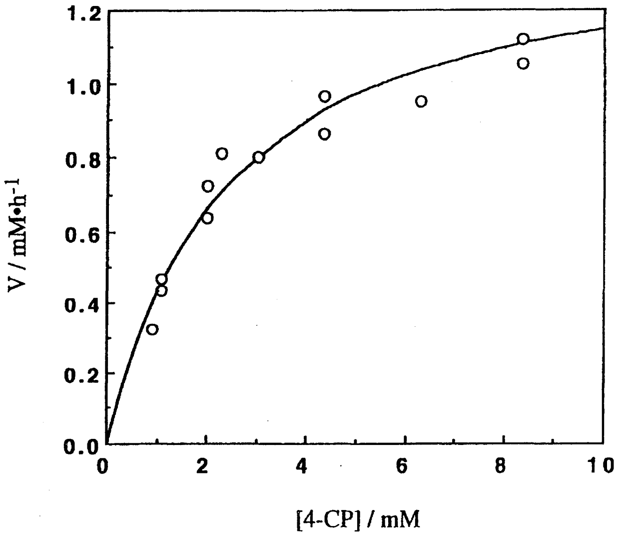

Fig. 2. Dependence of the initial rate of the photocatalytic decomposition ($\lambda > 340$ nm) of 4-chlorophenol catalyzed by $H_3PW_{12}O_{40}$ in aqueous solution on the concentration of 4-chlorophenol. [$H_3PW_{12}O_{40}$] = 0.5 mM; reaction temperature: 303 K. Other conditions are as described in the Experimental Section.

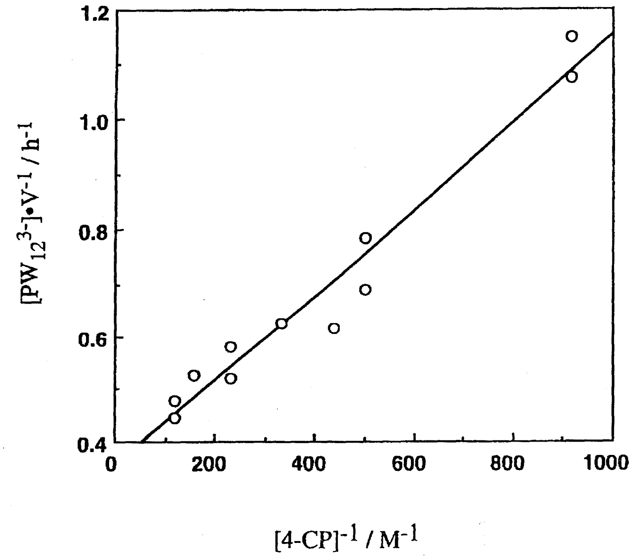

Fig. 3. Plot of $1/V\,(\mathrm{h}^{-1})$ vs. $1/[\text{4-chlorophenol}]\,(\mathrm{M}^{-1})$. V is the rate of the 4-chlorophenol photodecomposition.

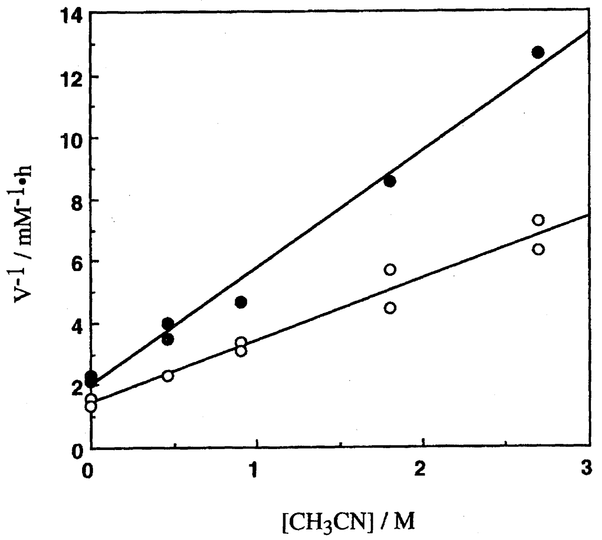

Fig. 4. Dependence of the initial rate of photocatalytic decomposition ($\lambda > 340$ nm) of 4-chlorophenol catalyzed by $H_3PW_{12}O_{40}$ in aqueous solution on the concentration of acetonitrile. V is the rate of the 4-chlorophenol photodecomposition. $[H_3PW_{12}O_{40}] = 0.5$ mM; [4-chlorophenol] = 1.0 (●), 2.0 mM (○). Reaction temperature: 303 K. Other conditions are as described in the Experimental Section.

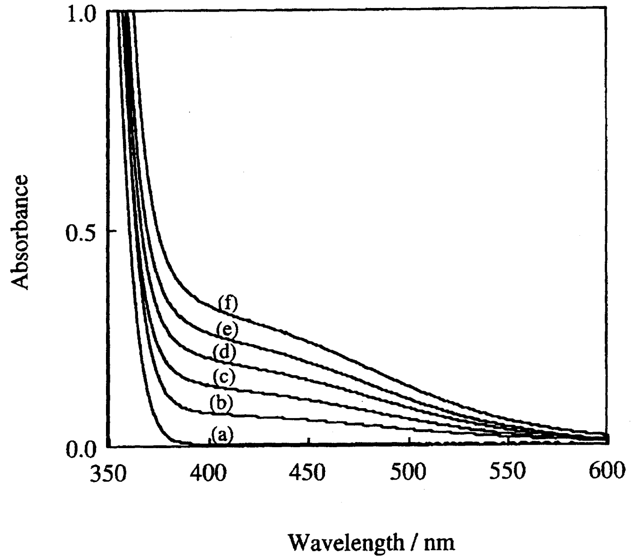

Fig. 5. Changes in the UV-vis absorption spectra (λ = 350—600 nm) of $H_3PW_{12}O_{40}$ in aqueous solution upon the addition of 4-chlorophenol. $[H_3PW_{12}O_{40}] = 25.0$ mM; [4-chlorophenol] = (a) 0, (b) 50, (c) 100, (d) 142, (e) 204, and (f) 250 mM. A cell with 1 cm path length was used.

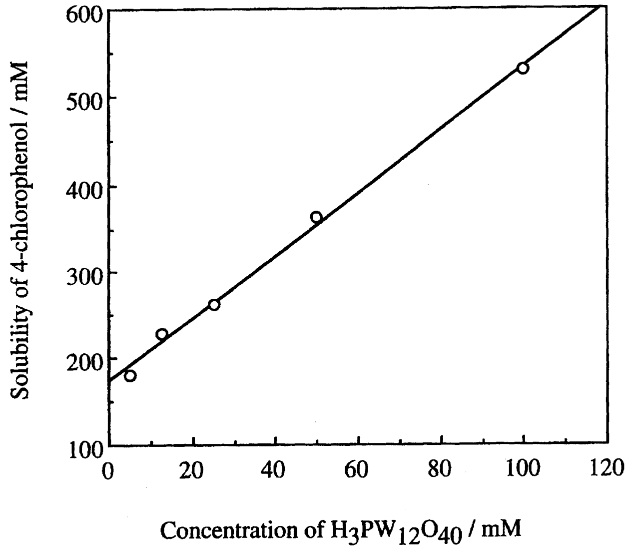

Fig. 6. Dependence of the solubility of 4-chlorophenol into water at 295 K on the concentration of $H_3PW_{12}O_{40}$.

region of 340—650 nm. Typical spectra are shown in Fig. 5. The absorbance of the band increased with an increase in the concentration of 4-chlorophenol. A similar increase was observed when the concentration of $PW_{12}{}^{3-}$ increased. In this region, there is no absorption band assignable to either 4-chlorophenol or $PW_{12}{}^{4-}$, the reduced heteropolyanion. $PW_{12}{}^{4-}$ has two bands at $\lambda_{max} = 498$ and 750 nm.[11] When the solution was analyzed by ^{1}H, ^{13}C NMR and HPLC, nothing but 4-chlorophenol was observed. Neither degraded compounds nor polymerized products were detected. In addition, ^{31}P NMR spectrum of the solution showed that the heteropolyanion, $PW_{12}{}^{3-}$, is intact and other heteropolytungstate such as a lacunary polyanion $PW_{11}O_{39}{}^{7-}$, or a Dawson-type heteropolytungstate, $PW_{18}O_{62}{}^{6-}$, were not detected. The changes in the spectra shown in Fig. 5 are very similar to the results reported by Hill et al.[3c,12,13,15] They observed that the low-energy portion of the oxygen-to-metal CT band varied due to the complexation with solvents,[3c,12,13,15] while ^{31}P NMR showed no change.

Therefore, the band in the 340—650 region is likely due to the formation of a complex between $PW_{12}{}^{3-}$ and 4-chlorophenol. When the light shorter than 420 nm in wavelength was irradiated, the 4-chlorophenol decomposition proceeded, although the rate was much lower.

Figure 6 shows the dependence of the solubility of 4-chlo-

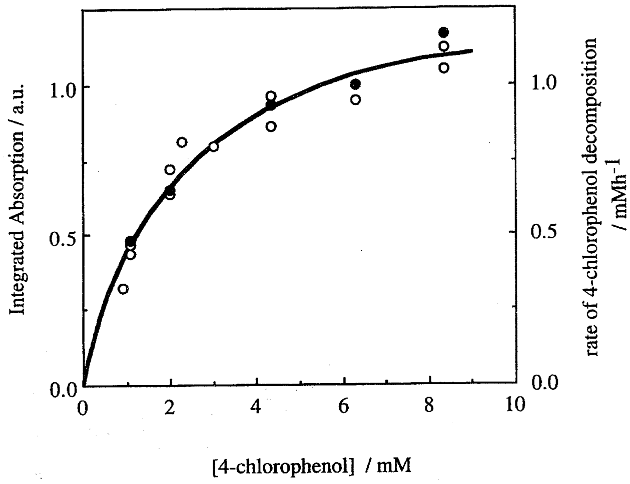

Fig. 7. Dependence of the integrated absorption (340—500 nm) of the aqueous solution containing $H_3PW_{12}O_{40}$ (0.5 mM) and 4-chlorophenol (0—8.4 mM) (●) and the rate of the 4-chlorophenol photodecomposition (○) on the concentration of 4-chlorophenol.

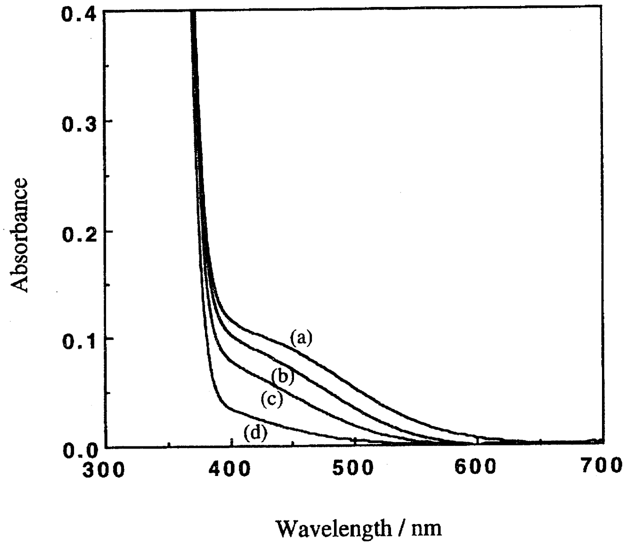

Fig. 8. Dependence of the UV-vis absorption spectrum (λ = 300—700 nm) of $H_3PW_{12}O_{40}$ in aqueous solution on the concentration of MeCN. $[H_3PW_{12}O_{40}]$ = 6.5 mM; [4-chlorophenol] = 16.5 mM; [MeCN] = (a) 0, (b) 1.6, (c) 3.2, and (d) 6.4 M.

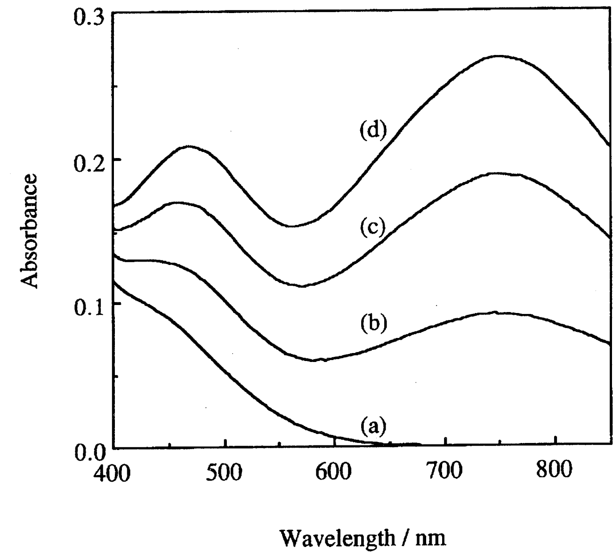

Fig. 9. Changes in the UV-vis absorption spectra (λ = 400—850 nm) of $H_3PW_{12}O_{40}$ upon irradiation (λ > 360 nm) of the aqueous solution containing 6.5 mM of $H_3PW_{12}O_{40}$ and 16.5 mM of 4-chlorophenol under deaerated conditions at 5 min intervals (t = 0—15 min). (a) 0, (b) 5, (c) 10, and (d) 15 min. A cell with 1 cm path length was used.

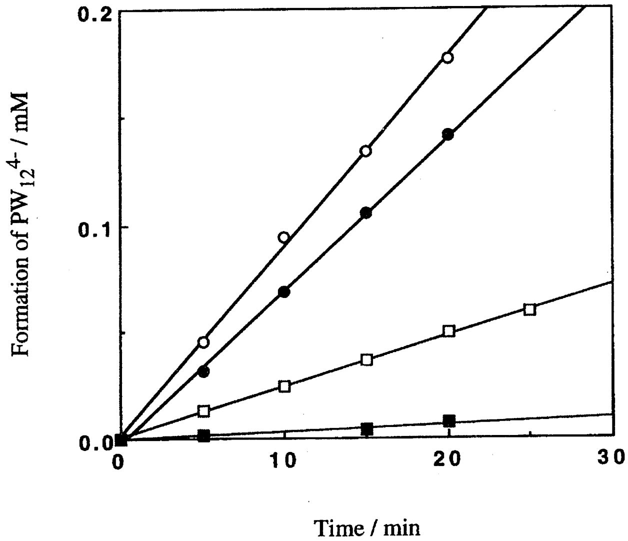

Fig. 10. Time courses for the formation of $PW_{12}O_{40}^{4-}$ upon irradiation (λ > 360 nm) of the aqueous solution containing 6.5 mM of $H_3PW_{12}O_{40}$ and 16.5 mM of 4-chlorophenol under deaerated condition. [MeCN] = 0 (○), 1.6 (●), 3.2 (□), and 6.4 M (■).

rophenol in water on the concentration of PW_{12}^{3-}. Interestingly, the solubility of 4-chlorophenol linearly increased as the concentration of PW_{12}^{3-} increased.

The spectral change in the visible region as shown in Fig. 5 was observed over a wide range of the concentration of heteropolyanion and 4-chlorophenol. For instance, even under the very diluted conditions ($[PW_{12}^{3-}]$ = ca. 0.5 mM, [4-chlorophenol] = ca. 10.0 mM), similar spectral changes were observed.

The integrated area of the new UV-vis absorption band increased in parallel with the rate of 4-chlorophenol decomposition when the concentration of 4-chlorophenol was increased, as shown in Fig. 7. The areas of the new bands were determined by integrating all the absorbance at each wavelength, as was done by Hill et al.[3d] The close relationship between the rate and new band is evident from the plots in Fig. 7.

The new band in the visible region changed depending on the concentration of acetonitrile as well. Typical spectra are shown in Fig. 8. The absorption of the band was decreased with increasing acetonitrile concentration. When the irradiation was carried out for these solutions under the deaerated conditions, the color of the solutions changed to blue, and a

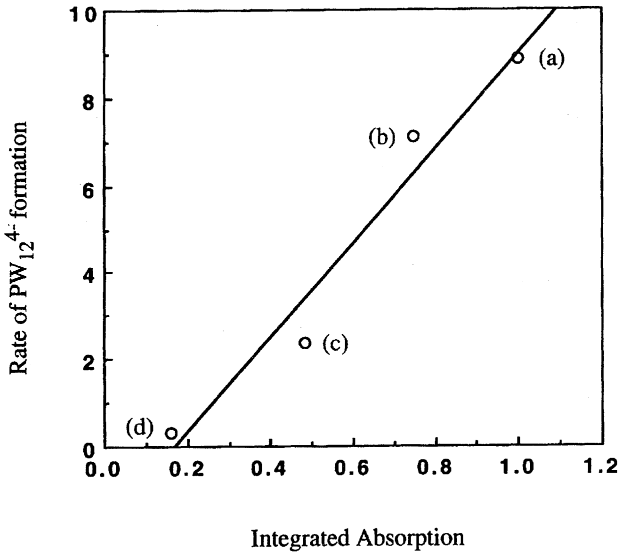

Fig. 11. Plot of the rate of the formation of $\mathrm{PW_{12}O_{40}}^{4-}$ vs. the integrated absorption (λ = 340—500 nm) of the aqueous solution containing $\mathrm{H_3PW_{12}O_{40}}$ (6.5 mM), 4-chlorophenol (16.5 mM) and MeCN (0—6.4 M). [MeCN] = (a) 0, (b) 1.6, (c) 3.2, and (d) 6.4 M.

new absorption band which is assignable to the inter-valence charge transfer band of $\mathrm{PW_{12}}^{4-}$, the one-electron reduced heteropolyanion, was observed at 400—850 nm in accordance with the literature[11] (Fig. 9). Figure 10 shows the time courses for the formation of $\mathrm{PW_{12}}^{4-}$ upon irradiation. The initial rate of $\mathrm{PW_{12}}^{4-}$ formation was dependent on the acetonitrile concentration.

In Fig. 11, the rate of the formation of $\mathrm{PW_{12}}^{4-}$ shown in Fig. 10 is plotted against the integrated area of the new band shown in Fig. 8. An approximately linear correlation was obtained.

Discussion

In the previous study, in which a 320 nm filter was used to imitate the solar light, 4-chlorophenol was decomposed to some extent even in the absence of the catalyst. A UV-34 filter was adopted in the present study in order to avoid the direct photolysis to further clarify the reaction mechanism. In both cases, the behavior of the catalysts was essentially the same. For instance, the rates were similar and the main products in the initial stage were hydroquinone and 4-chlorocatechol, which were further decomposed by photoactivated $\mathrm{PW_{12}}^{3-}$ within several hours also in the present case. It is possible that the direct photolysis became almost negligible in the presence of the catalyst, possibly due to the absorption of light by $\mathrm{PW_{12}}^{3-}$ (inner filter effect).

We previously reported that the photodecomposition of 4-chlorophenol catalyzed by $\mathrm{PW_{12}}^{3-}$ using the 320 nm filter consists of the photoreduction and the reoxidation steps.[10] We proposed that there is precomplexation between the heteropolyanion and 4-chlorophenol, as described in Eqs. 1, 2, 3, 4, and 5, since the reaction rates obeyed the Langmuir–Hinshelwood type kinetics.[10]

$$\mathrm{PW_{12}}^{3-} + \text{4-CP} \overset{K}{\rightleftarrows} \mathrm{PW_{12}}^{3-}\cdot\text{4-CP} \tag{1}$$

$$\mathrm{PW_{12}}^{3-}\cdot\text{4-CP} \xrightarrow[h\nu]{I\Phi} \mathrm{PW_{12}}^{3-*}\cdot\text{4-CP} \tag{2}$$

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

$$\mathrm{PW_{12}}^{3-*}\cdot\text{4-CP} \xrightarrow{k_1} \mathrm{PW_{12}}^{4-} + \begin{matrix}\text{hydroquinone}\\ \text{4-chlorocatechol}\end{matrix} \tag{4}$$

$$\mathrm{PW_{12}}^{4-} + \mathrm{O_2} \xrightarrow{\text{fast}} \mathrm{PW_{12}}^{3-} + \mathrm{O_2}^{-} \tag{5}$$

$$[\mathrm{PW_{12}}^{3-}]_0 V^{-1} = \frac{1}{k'}\left(1 + \frac{1}{K[\text{4-CP}]_0}\right)$$
$$k' = I\Phi k_1/(k_1 + k_{\mathrm{ic}}) \quad \text{4-CP : 4-chlorophenol,} \tag{6}$$

Here, K refers to the equilibrium constant, I the quantity of light absorbed, Φ the quantum efficiency for the production of the excited state, k_1 the rate constant for the redox reaction of the excited state of the complex, and k_{ic} the rate constant for deactivation of the excited state. According to this mechanism, the rate of the 4-chlorophenol photodecomposition, V, can be described by Eq. 6. Here $[\mathrm{PW_{12}}^{3-}]_0$ and $[\text{4-CP}]_0$ are the initial concentrations of the catalyst and 4-chlorophenol, respectively. In the present study in which UV-34 was used as the cut-off filter, the reaction rate followed essentially the same kinetics. From the reciprocal plot shown in Fig. 3, the equilibrium constant K was calculated to be $4.5\times10^2\ \mathrm{M^{-1}}$. This was close to the value ($6.9\times10^2\ \mathrm{M^{-1}}$) obtained in the previous study in which a UV-32 filter was used.

One may point out another possible mechanism, that is: the diffusional encountering mechanism, in which the photoexcited polyanion encounters 4-chlorophenol to form an exciplex (Eq. 9) and subsequently 4-chlorophenol is decomposed.

$$\mathrm{PW_{12}}^{3-} \xrightarrow[h\nu]{I\Phi} \mathrm{PW_{12}}^{3-*} \tag{7}$$

$$\mathrm{PW_{12}}^{3-*} \xrightarrow{k_{\mathrm{ic}}} \mathrm{PW_{12}}^{3-} \tag{8}$$

$$\mathrm{PW_{12}}^{3-*} + \text{4-CP} \xrightarrow[(\mathrm{PW_{12}}^{3-}\cdot\text{4-CP})]{k_1} \mathrm{PW_{12}}^{4-} + \begin{matrix}\text{hydroquinone}\\ \text{4-chlorocatechol}\end{matrix} \tag{9}$$

$$[\mathrm{PW_{12}}^{3-}]_0 V^{-1} = \frac{1}{I\Phi}\left(1 + \frac{k_{\mathrm{ic}}}{k_1[\text{4-CP}]}\right) \tag{10}$$

In this case, the reaction rate, V, can be described by Eq. 10, according to the reactions (7)—(9). However, when the rate constant k_1 is evaluated from the reciprocal plot in Fig. 3 and the lifetime of the excited state of $\mathrm{PW_{12}}^{3-}$ in water[3d] (1.5±0.5 ns), the values of k_1 becomes 30-fold greater than the bimolecular diffusion control limit (10^{10}).[14] Therefore, the diffusional encountering mechanism is not probable in the present case.

The effect of acetonitrile addition in the solution also supports the Langmuir–Hinshelwood mechanism. It was reported that complexation between $\mathrm{PMo_{12}O_{40}}^{3-}$ and *N*,*N*-dimethylacetamide was suppressed in the acetonitrile solution.[12] There can be inhibition of acetonitrile (MeCN) by the competitive complexation with the heteropolyanion, as described in Eq. 11. Then, the reaction rate can be described as in Eq. 12, where K' stands for the equilibrium constant of the complexation of acetonitrile.

$$\mathrm{PW_{12}}^{3-} + \mathrm{MeCN} \overset{K'}{\rightleftharpoons} \mathrm{PW_{12}}^{3-}\cdot\mathrm{MeCN} \tag{11}$$

$$[\mathrm{PW_{12}}^{3-}]_0 V^{-1} = \frac{1}{k'}\left(1 + \frac{1}{K[\text{4-CP}]_0} + \frac{K'[\mathrm{MeCN}]}{K[\text{4-CP}]_0}\right) \tag{12}$$

The good linearity obtained in Fig. 4 indicates that this mechanism is plausible. Moreover, when the equilibrium constants K' are calculated for each concentration of 4-chlorophenol, the value were nearly constant ($K'=2.5\pm0.05$). On the other hand, the diffusional encountering mechanism as discussed above can not explain the effect of acetonitrile addition. The lifetime of the excited state of $\mathrm{PW_{12}}^{3-}$ in acetonitrile is almost identical with that in water,[3d] indicating that acetonitrile does not act as a quencher. The diffusion rate of $\mathrm{PW_{12}}^{3-}$ in acetonitrile, which is evaluated from the Stokes–Einstein equation,[16] is greater than that in H_2O (viscosity: acetonitrile, 0.375; H_2O, 1.002 [mM sm^{-2}], respectively[17]), predicting that the bimolecular encountering would be more frequent in acetonitrile than in water.

Spectroscopic evidence for the complexation between the heteropolyanion and organic compounds has been reported. Pope et al. investigated the interaction between the Keggin-type heteropolyanion and hydrated chloral by ^{1}H NMR.[18] Fox et al. reported, based on NMR and fluorescence lifetime measurements, that $\mathrm{PW_{12}}^{3-}$ coordinates with alcohols.[3d] Hill et al. showed that there was interaction between tetramethylurea and $\mathrm{PMo_{12}O_{40}}^{3-}$ by means of X-ray structural analysis and UV-vis spectroscopy.[12]

In the present study, the UV-vis absorption spectrum of heteropolyanion changed by the complexation between $\mathrm{PW_{12}}^{3-}$ and 4-chlorophenol as discussed above. The spectral change due to the complex formation may be rationalized by the Mulliken's electron donor–acceptor (EDA) complex. The applicability of this concept to the polyanion–organic molecule was discussed by Hill.[3c,15] The assignment of the new band in the visible range (Fig. 5) to the complexation is supported by the following facts: 1) the solubility of 4-chlorophenol into water increased in the presence of $\mathrm{PW_{12}}^{3-}$ (Fig. 6) and 2) the absorption band was suppressed by the presence of acetonitrile, as shown in Fig. 8. This type of new band may be attributed to the intramolecular oxygen-to-metal charge-transfer transition or the outer-sphere charge-transfer transition.[3c]

It was reported that the rate equation for the hydration of isobutene with $H_4SiW_{12}O_{40}$ was dependent on the catalyst concentration and the interaction between the heteropolyanion and the substrate became strong in a concentrated solution.[19] In the present study, the interaction between the heteropolyanion and 4-chlorophenol was observed even in a dilute solution.

It is concluded as described below that this polyanion–4-chlorophenol complex observed spectroscopically is really responsible for the photoreaction. First, good correlation was obtained between the rate of photoreaction and the degree of the complex formation, as shown in Fig. 7. Second, the addition of acetonitrile caused the suppression of both the reaction rate and the complex formation. A good correlation as in Fig. 3 can be obtained in this case, too. The third piece of evidence is the kinetic plot in Fig. 11. This plot shows that the rate of reduction of $\mathrm{PW_{12}}^{3-}$ to $\mathrm{PW_{12}}^{4-}$ by irradiation under deaerated conditions is directly correlated with the intensity of the new band, or the degree of the complex formation. The linear plot in Fig. 11 indicates that the $\mathrm{PW_{12}}^{4-}$ formation, which is the rate-determining step for the 4-chlorophenol photodecomposition according to our previous work,[10] parallels the degree of the $\mathrm{PW_{12}}^{3-}$–4-chlorophenol complex formation.

Conclusion

Kinetic and spectroscopic evidence confirmed the Langmuir–Hinshelwood type mechanism for the photodecomposition of 4-chlorophenol catalyzed by $\mathrm{PW_{12}}^{3-}$; there is precomplexation between heteropolyanion and 4-chlorophenol before photoreaction of 4-chlorophenol proceeds. The complex formation was supported by the appearance of a new UV-vis band at 340—650 nm and the linear correlation between the rate of photoreaction and the band intensity. This mechanism is consistent with that of the alcohol photooxidation catalyzed by $\mathrm{PW_{12}}^{3-}$. The high affinity for organic compounds may be one of the remarkable characteristics of $\mathrm{PW_{12}}^{3-}$.

The present study may be extended in the following directions for application, taking advantages of heteropoly compounds: 1) Usage of insoluble heteropoly compounds, e. g., cesium salt of 12-tungstophosphoric acid, and 2) enhancement of the efficiency in the visible light region by changing the constituent elements.

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