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Catalysis of Polyvinylpyridine-Supported Cu(II) during 2,6-Di-*tert*-Butylphenol Oxidation in the Presence of Inorganic Base

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The liquid-phase oxidation of 2,6-di-*tert*-butylphenol(BOH) was studied using a heterogeneous polymer-supported Cu(II) catalyst, basic Cu(II)–poly(4-vinylpyridine) (Cu(II)–PVP) catalyst. The only oxidation product was 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone. The oxidation reaction of BOH did not proceed by the presence of only the Cu(II)–PVP catalyst itself, but was significantly promoted by adding an inorganic base such as KOH in the solvent. The added KOH was found to have the role of generating the corresponding phenolate anion by dissociating the BOH molecule. The turnover number (mole of absorbed O_2 molecule per unit time and unit mole of Cu(II)) with the basic Cu(II)–PVP catalyst in the BOH oxidation passed through a maximum with the variation in the pyridine/Cu(II) mole ratios (ligand ratio). From the dependence of the reaction rate on the Cu(II) concentration of the Cu(II)–PVP catalyst, it was found that the reaction order of the Cu(II) concentration was changed from second- to first-order with an increase in the Cu(II) amount in the Cu(II)–PVP. On the basis of the kinetic results it is assumed that the rate-determining step in the BOH oxidation catalyzed by the basic Cu(II)–PVP changed from the reoxidation step of the dinuclear Cu(I) complex with an oxygen molecule to the BOH oxidation step by the mononuclear Cu(II) complex with an increase in the Cu(II) amount in the Cu(II)–PVP catalyst. Since the catalytic activity of the used Cu(II)–PVP catalyst almost remained intact, it was found possible to re-use the Cu(II)–PVP catalyst. © 1992 Academic Press, Inc.

INTRODUCTION

Some attempts to heterogenize a homogeneous catalyst, which has a high catalytic activity and selectivity, have been studied in order to facilitate the after-treatment of the reaction system, such as separation of the catalyst from the product (*1–3*). The general method for heterogenization is to fix the homogeneous catalyst on an organic (*4–9*) and/or inorganic (*10*) supports. As an organic support, polyvinylpyridine (PVP) has been frequently used (*11, 12*) because of its chemical stability and insolubility in an organic solvent. The Cu(II)–PVP complex has been found (*13*) to become an effective catalyst for the oxidation of 3,5-di-*tert*-butylcatechol.

The oxidative coupling reaction of phenol derivatives catalyzed by copper–amine complexes is one of the interesting reaction systems from the point of view of the mimic of a copper-contained biological system, in addition to that from an organic synthetic point of view. The copper catalytic systems for the oxidative coupling of phenols have been developed since Hay and his group reported the synthesis of polyphenylene oxide, one of the important engineering plastics, through the oxidative coupling polymerization of 2,6-dimethylphenol catalyzed by a copper–pyridine complex (*14–17*). We have also reported (*18, 19*) that the basic copper(II) system ($CuCl_2$–KOH system) without an organic amine such as pyridine was an effective catalyst for the oxidative coupling reaction of 2,6-dimethylphenol. This heterogeneous basic copper(II) catalytic system was found to homogenize in the process of the liquid-phase oxidative coupling reaction of phenols, from which results we called this

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basic copper(II) catalyst as a "heterogenized homogeneous catalyst."

In this study, we report the oxidative coupling reaction of 2,6-di-*tert*-butylphenol catalyzed by a heterogeneous Cu(II)–PVP complex with a base such as KOH. The influences of the kind and amount of the base used, the concentration of Cu(II) ion in the PVP, and the ligand ratios (pyridine group in PVP/Cu(II) mole ratio) on the catalytic activity for the phenol oxidation have been systematically investigated in order to clarify the nature of the oxidation ability of the Cu(II)–PVP complexes. From the kinetic results, the concentration of Cu(II) ions in the PVP was found to have an important role in the phenol oxidation, thus affecting the rate-determining step of the phenol oxidation reaction.

EXPERIMENTAL

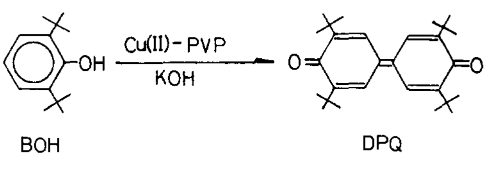
Reagents. 2,6-Di-*tert*-butylphenol (BOH) was purchased from Nacalai Tesque (guaranteed reagent) and used after recrystallization from *n*-hexane. Methanol and chloroform were used without further purification (Nacalai Tesque, extra pure-grade). Pyridine, KOH, NaOH (Nacalai Tesque, guaranteed-grade), methanolic solution of 30% $NaOCH_3$ (Nacalai Tesque, extra pure-grade), and $NaNO_3$ (Wako Chemical Co., extra pure-grade) were all used without further purification. Poly(4-vinylpyridine) (Aldrich Chemical Co., lot no. 06105LL) and poly(4-vinylpyridine-co-stylene) (stylene 10%) (Aldrich Chemical Co., lot no. 80148JP) were used without further purification.

Catalysts. $CuCl_2$, $CuBr_2$, $Cu(NO_3)_2 \cdot 3H_2O$, $Cu(CH_3COO)_2 \cdot H_2O$ (Nacalai Tesque, guaranteed reagent), bis(acetylacetonato) $Cu(II) \cdot 3H_2O$ ($Cu(acac)_2$) (Nacalai Tesque, extra pure-grade), and $CuSO_4 \cdot 5H_2O$ (Wako Chemical Co., guaranteed reagent) were used without further purification. Bis(ethylacetoacetato) Cu(II) ($Cu(acest)_2$), bis(dimethylglyoximato) Cu(II) ($Cu(dmg)_2$), bis(acetylacetone)ethyleneiminoato Cu(II) (Cu(acacen)) were synthesized by conventional methods (*20–22*). Cu(II)–poly-(4-vinylpyridine) (Cu(II)–PVP) was prepared as follows: A 2.1 g sample of poly(4-vinylpyridine) (PVP) and 5 mmol of $CuCl_2$ were added to 50 cm^3 of methanol and mixed using a mechanical stirrer at 373 K for 30 min, filtered off, washed with methanol, and dried at room temperature. $CuBr_2$, $Cu(NO_3)_2 \cdot 3H_2O$, $Cu(CH_3COO)_2 \cdot H_2O$, $CuSO_4 \cdot 5H_2O$, and $Cu(dmg)_2$ were anchored to PVP using the method similar to $CuCl_2$. $Cu(acac)_2$, $Cu(acest)_2$, $Cu(salad)_2$, and Cu(acacen) were anchored to PVP using $CHCl_3$ solvent in the place of methanol solvent. Cu(II)–poly(4-vinylpyridine-co-styrene: styrene 10%) was prepared using the same manner previously described, with $CuCl_2$ in deionized water solvent. The amounts of the Cu(II) ions anchored in the PVP support were varied by changing the Cu(II) concentration of the Cu(II) solution. The KOH-impregnated Cu(II)–PVP catalyst was prepared by dispersing the Cu(II)–PVP in the methanolic KOH solution and vaporizing the solvent while stirring. The Cu(II) ions anchored and/or K^+ ions impregnated in the PVP supports were quantitatively measured using an atomic absorption method after dissolving the corresponding catalysts in diluted HCl aqueous solution.

Oxidation of 2,6 - di - tert - butylphenol (BOH). The oxidation reaction of BOH catalyzed by the Cu(II)–PVP system with base such as KOH was performed using conventional constant-pressure-type gas absorption equipment with a gas buret and connected to a vacuum line. The standard reaction condition was as follows: BOH, 5.0×10^{-2} mol/liter; 50 cm^3 of mixed solvent containing CH_3OH and $CHCl_3$ ($CH_3OH/CHCl_3$ = 7/3 vol%); reaction temperature, 303 K; oxygen pressure, 1 atm. The heterogeneous Cu(II)–PVP catalyst and 40 ml of the mixed solvent were added to a two-necked glass reactor which was connected to the gas absorption equipment, and BOH and 10 ml^3 of the mixed solvent were added to a dropping funnel which was connected to the reactor. After the gas absorption equipment was purged with pure oxygen (1 atm), the BOH solution in the dropping funnel was quickly added to the catalytic solution in the reactor, which was considered the starting time of the oxidation. The amount of oxygen absorption was measured through a gas-buret which is accurate to 0.1 cm^3. The initial rate of oxygen absorption was obtained by least-square plots (5–7 plots) of the relationship between the oxygen absorption amount vs reaction time. The concentrations of the oxidation product (3,3'.5.5-tetramethyl-4,4'-diphenoquinone) at every time interval were measured by the electronic absorption spectra (Shimazu-type UV-240, λ_{max} = 422 nm in the mixed $CH_3OH + CHCl_3$ solvent). The oxidation product was identified as 3,3',5,5'-tetramethyl-4,4'-diphenoquinone by IR spectroscopy (Analect Instruments Model FX-6200 FT-IR). The quantitative analysis of the hydrogen peroxide produced during the oxidation was determined by conventional iodometry (*23*).

RESULTS

Dark-red crystals were obtained as the only oxidation product of 2,6-di-*tert*-butylphenol (BOH) catalyzed by the base added Cu(II)–PVP system. The product was identified as 3,3,'5,5'-tetra-*tert*-butyl-4,4'-diphenoquinone (DPQ) based on a comparison with the IR spectrum of the authentic DPQ which was synthesized from the oxidation of BOH catalyzed by a copper(II) nitrate–acetonitrile system (24):



As for the stoichiometry of the BOH oxidation with an oxygen molecule, the following two equations are considered:

$$BOH + \tfrac{1}{2}O_2 = \tfrac{1}{2}DPQ + H_2O \qquad (1)$$

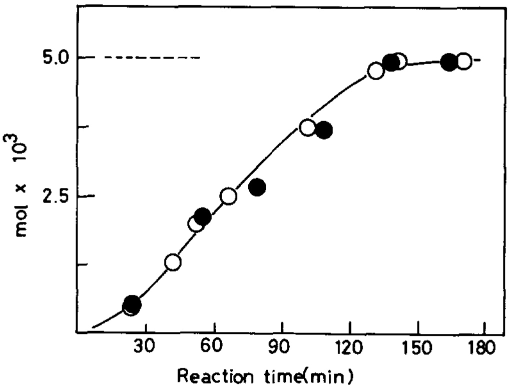


FIG. 1. Time dependence of the amounts of O_2 absorption and formed DPQ: BOH, 2.0 × 10^{-2} *M*; Cu(II)–PVP (pyridine unit in PVP/Cu(II) = 10), 0.25 g; KOH (in reaction solution), 1.78 × 10^{-2} *M*; KOH/Cu(II) mole ratio, 5; solvent, CH_3OH(35 cm^3) + $CHCl_3$(15 cm^3); temp., 303 K; ●, amount of formed DPQ; ○, amount of absorbed O_2; ———, theoretical O_2 or BOH calculated on the basis of $BOH + \frac{1}{2} O_2 = \frac{1}{2} DPQ + H_2O$.

$$BOH + O_2 = \tfrac{1}{2}DPQ + H_2O_2. \qquad (2)$$

Figure 1 illustrates the relationship between both the DPQ amount yield and the oxygen absorption amount vs reaction time. The oxygen absorption amount (mole number) at some reaction time was found to equal nearly one-half of the corresponding DPQ mole number produced. The H_2O_2 accumulation until the reaction time at which a 100% yield of DPQ was obtained was found to be less than 10% of the calculated value based on Eq. (2). From these results, it is reasonable to consider Eq. (1), in which no accumulation of H_2O_2 is observed during the oxidation, as the main stoichiometry of the oxidation of BOH to DBQ, though the partial participation of the stochiometry, Eq. (2), cannot be denied.

Effect of mixed solvent. The effect of the volume fraction of $CHCl_3$ in the mixed solvent of CH_3OH and $CHCl_3$ on the oxidation rate in the BOH oxidation catalyzed by the base added Cu(II)–PVP system is shown in Fig. 2. The volume fraction of about 30% $CHCl_3$ had the maximum activity. We have hereafter used the mixed

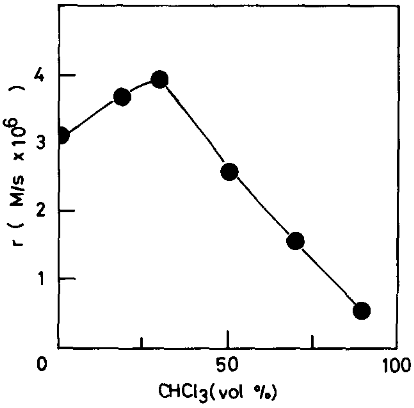


FIG. 2. Influence of chloroform component in the methanol and chloroform mixed solvent on the reaction rate: BOH, 5.0×10^{-2} *M*; Cu(II)–PVP (pyridine unit in PVP/Cu(II) = 10), 0.25 g; KOH (in reaction solution), 1.1×10^{-2} *M*; KOH/Cu(II) mole ratio, 2.5; temp., 303 K.

TABLE 1

BOH Oxidation Catalyzed by Cu(II)–PVP and KOH[a]

Catalytic system	Reaction rate (mol/(liter · s) × 10^6)
KOH only	0
Cu(II)–PVP only	0
Cu(II)–PVP + KOH added in the catalytic solution	23.5
Cu(II)–PVP + KOH added in the BOH solution	24.1
Cu(II)–PVP + potassium di-*tert*-butylphenolate isolated	26.7
KOH_{imp}–CU(II)–PVP	2.52

[a] BOH, 5.0×10^{-2} *M*; KOH, 5.0×10^{-2} *M*, Cu(II)–PVP, 0.25 g; pyridine group in PVP/Cu(II) mole ratio, 13; solvent, CH_3OH(35 cm^3) + $CHCl_3$(15 cm^3).

solvent of $CH_3OH/CHCl_3$ = $\frac{7}{3}$ vol% for the oxidation of BOH.

Effect of the particle size of the Cu(II)–PVP catalyst. No effect of catalyst particle size on the oxidation rate was observed, from the relationship between the oxidation rate of BOH vs the average particle size of the Cu(II)–PVP. The resistance of pore diffusion in the Cu(II)–PVP particles was thereby found to be negligible under the reaction conditions studied here. The Cu(II)–PVP with an average particle size ($\overline{dp}$) of 37 μm (0–200 mesh) was used as the catalyst in this study.

Effect of the base added in the reaction solution. The addition of base produced comparatively similar rates in the oxidation of BOH, regardless of the kind of the base used in this study (KOH, NaOH, $NaOCH_3$, $NaOC_2H_5$, $NaOC_4H_9$, and KOC_4H_9). The addition of $NaNO_3$ had no oxidation activity. Table 1 shows the effect of the method of addition of KOH on the oxidation rate of BOH. The catalytic activity of the KOH-impregnated Cu(II)–PVP (KOH_{imp}–Cu(II)–PVP) catalyst was ca. one-tenth of that of the Cu(II)–PVP + KOH catalytic system, in which KOH in both systems was held at the same value. Figure 3 illustrates the influence of the KOH amount on the oxidation rate of BOH at a constant concentration of Cu(II)–PVP catalyst. The rate increased with an increase in the KOH concentration in the region of the lower KOH concentrations, but leveled off at the higher KOH concentrations.

Effect of the Cu(II)–PVP. Table 2 shows the influence of the Cu(II) precursor in the Cu(II)–PVP catalyst on the turnover number (the number of moles of DPQ formed

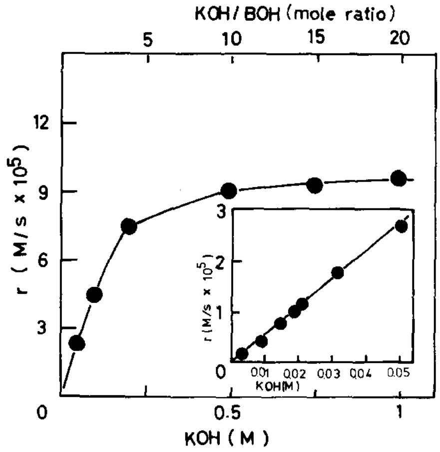


FIG. 3. Influence of the KOH concentration on the reaction rate: BOH, 5.0×10^{-2} *M*; Cu(II)–PVP (pyridine unit in PVP/Cu(II) = 11), 0.25 g; solvent, CH_3OH(35 cm^3) + $CHCl_3$(15 cm^3); temp., 303 K.

TABLE 2

Effect of Cu(II) Precursor in the Cu(II)–PVP[a]

Cu(II) precursor in Cu(II)–PVP	KOH/Cu(II)	Pyridine unit in PVP/Cu(II)	Turnover number (mol product/(s Cu(II)) × 10^4)
$CuCl_2$	2.5	33	7.5
$Cu(CH_3COO)_2$	2.5	28	8.5
$CuBr_2$	2.5	20	5.5
$Cu(NO_3)_2$	2.5	44	6.0
$CuSO_4$	2.5	26	7.0
$Cu(acac)_2$	48.0	252	95.0
$Cu(acest)_2$	10.0	54	38.5
$Cu(salad)_2$	4.0	28	14.0
$Cu(dmg)_2$	2.2	11	0.5
Cu(acacen)	310.0	1500	0

[a] BOH, 5.0×10^{-2} *M*; Cu(II)–PVP, 0.25 g; KOH, 8.92×10^{-3} *M*; solvent, CH_3OH(35 cm^3) + $CHCl_3$(15 cm^3).

per mole of Cu(II) and in unit time). The difference in the turnover numbers of the simple Cu(II) salts used as a precursor was found not to be high, however, the turnover numbers of Cu(II) chelate complexes, such as $Cu(acac)_2$, used as a precursor had a comparatively broad range of values. Figure 4 illustrates the effect of the amount of Cu(II)–PVP on the oxidation rate using the concentration of KOH as a parameter. The increase in the KOH concentration caused an increase in the oxidation rates. The oxidation rates sharply increased in the region of low amounts of Cu(II)–PVP and passed through a maxima, irrespective of the KOH concentration. It must be also noted that the maximum rates are obtained at a KOH/Cu(II) mole ratio of ca. 5, irrespective of the KOH concentration. Figure 5 shows the effect of the Cu(II)–PVP amount at constant KOH/Cu(II) mole ratios on the oxidation rate. The oxidation rate increased almost linearly with an increase in the weight of the Cu(II)–PVP.

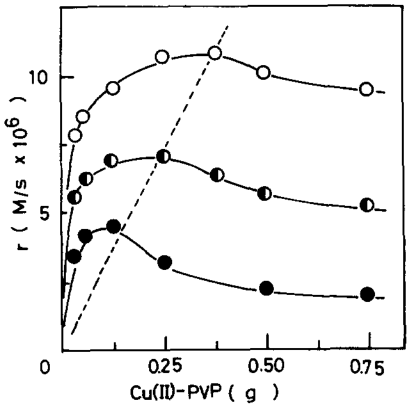


FIG. 4. Influence of the weight of the Cu(II)–PVP catalyst on the reaction rate at constant KOH concentration: BOH, 5.0×10^{-2} *M*; Cu(II)–PVP (8.94×10^{-4} Cu(II) mol/g), pyridine unit in PVP/Cu(II) = 13; solvent, CH_3OH(35 cm^3) + $CHCl_3$(15 cm^3); temp., 303 K; ———, plots at the mole ratio of KOH to Cu(II) = 5; ○, 2.67×10^{-2} *M* of KOH; ◐, 1.78×10^{-2} *M* of KOH; ●, 8.91×10^{-3} *M* of KOH.

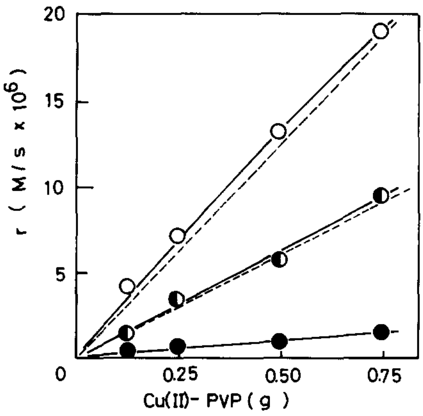


FIG. 5. Influence of the weight of the Cu(II)–PVP catalyst on the reaction rate at constant KOH to Cu(II) mole ratio: BOH, 5.0×10^{-2} *M*; Cu(II)–PVP, pyridine unit in PVP/Cu(II) = 9.0; solvent, CH_3OH(35 cm^3) + $CHCl_3$(15 cm^3); temp., 303 K; ○, mole ratio of KOH to Cu(II) = 5; ◐, mole ratio of KOH to Cu(II) = 2.5; ●, mole ratio of KOH to Cu(II) = 1.0; ———, calculated amount (see text).

KOH impregnated Cu(II)–PVP catalyst. In the place of the addition of KOH into the reaction solution, the effect of the KOH (KOH_{imp}) directly impregnated on the Cu(II)–PVP on the BOH oxidation was investigated in order to compare the two methods of KOH addition. The dependence of the oxidation rates catalyzed by the KOH_{imp}–Cu(II)–PVP systems without KOH in the reaction solution and with KOH

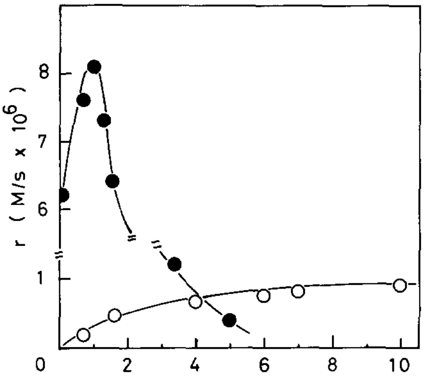


FIG. 6. Influence of the mole ratio of impregnated KOH to Cu(II) on the reaction rate: ○, without KOH in the reaction solution; BOH, 5.0×10^{-2} *M*; KOH_{imp}–Cu(II)–PVP (pyridine unit in PVP/Cu(II) = 9.8), 0.24 g; solvent, CH_3OH(35 cm^3) + $CHCl_3$(15 cm^3); temp., 303 K; ●, with KOH in the reaction solution; BOH, 5.0×10^{-2} *M*; KOH in the reaction solution, 1.34×10^{-2} *M*; KOH_{imp}–Cu(II)–PVP (pyridine unit in PVP/Cu(II) = 9.0), 0.25 g; solvent, CH_3OH(35 cm^3) + $CHCl_3$(15 cm^3); temp., 303 K.

in the reaction solution on the impregnated KOH amount (as KOH_{imp}/Cu(II) mole ratio at the constant amount of the Cu(II) ion) is illustrated in Fig. 6. The oxidation rates of the former KOH_{imp}–Cu(II)–PVP system without KOH in the reaction solution were found to be appreciably lower than those of the latter KOH_{imp}–Cu(II)–PVP system with KOH in the reaction solution. The oxidation rate of the KOH_{imp}–Cu(II)–PVP system without KOH in the reaction solution increased with an increase in the impregnated KOH amount and leveled off at with further increases in the impregnated KOH (Fig. 6). On the other hand, in the KOH_{imp}–Cu(II)–PVP catalytic system with KOH in the reaction solution, the oxidation rate increased with the KOH_{imp}/Cu(II) mole ratios, but passed through a maximum with further increases in the ratio and was inhibited with an excess amount of KOH_{imp} (Fig. 6). The oxidation rate in the presence of KOH in the reaction solution was found to almost increase linearly with the weight of the KOH_{imp}–Cu(II)–PVP catalytic system. The effect of the KOH concentration in the reaction solution on the oxidation rate was investigated in the Cu(II)–PVP and the KOH_{imp}–Cu(II)–PVP catalytic systems (Fig. 7). Both the Cu(II)–PVP and KOH_{imp}–Cu(II)–PVP (KOH_{imp}/Cu(II) mole ratio, 1.3) showed almost a similar dependence on the KOH concentration, though the rates of the latter catalytic system were always slightly higher (the amount of Cu(II) ions are almost similar in the both systems). However, the rate of the KOH_{imp}–Cu(II)–PVP catalyst for a KOH_{imp}/Cu(II) mole ratio of 7.0 was not strongly dependent on the KOH concentration, and the rate was found to be considerably lower than the one in the KOH_{imp}–Cu(II)–PVP for the KOH_{imp}/Cu(II) mole ratio of 1.3. It must be noted that the Cu species in the KOH_{imp}–Cu(II)–PVP with a KOH_{imp}/Cu(II) mole ratio of 1.3 were green in color, but the ones in the mole ratio of 7.0 were rather light-brown. This may suggest a change in the charge of the Cu

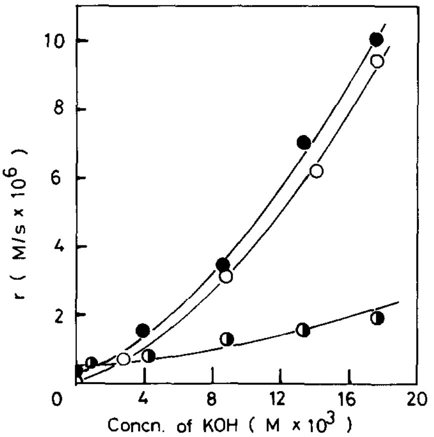


FIG. 7. Influence of the concentration of KOH in the reaction solution on the reaction rate: BOH, 5.0×10^{-2} *M*; solvent, CH_3OH(35 cm^3) + $CHCl_3$(15 cm^3); temp., 303 K; ○, Cu(II)–PVP (8.94×10^{-4} Cu(II) eq/g), 0.25 g; ◑, KOH_{imp}–Cu(II)–PVP (7.42×10^{-4} Cu(II) eq/g, KOH_{imp}/Cu(II) = 7.0), 0.39 g; ●, KOH_{imp}–Cu(II)–PVP (8.58×10^{-4} Cu(II) eq/g, KOH_{imp}/Cu(II) = 1.3), 0.275 g.

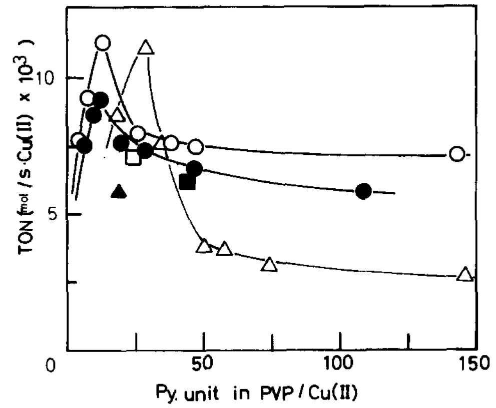


FIG. 8. Dependence of the oxidation activity of the Cu(II)–PVP catalysts on the ligand ratio: BOH, 5.0 × 10^{-2} *M*; Cu(II)–PVP, 0.25 g; mole ratio of KOH in the reaction solution to Cu(II), 2.5; solvent, CH_3OH (35 cm^3) + $CHCl_3$(15 cm^3); temp., 303 K; ●, $CuCl_2$ used as source of Cu(II) ions; ○, $Cu(CH_3COO)_2$ used as source of Cu(II) ions; △, Cu(II) (salad)$_2$ used as source of Cu(II) ions; □, $CuSO_4$ used as source of Cu(II) ions; ▲, $CuBr_2$ used as source of Cu(II) ions; ■, $Cu(NO_3)_2$ used as source of Cu(II) ions.

species from Cu(II) to Cu(I) due to the excess KOH impregnated on the PVP.

Effect of ligand ratio. The effect of the ligand ratio (mole ratio of pyridine units in PVP to Cu(II)) on the turnover number (TON) was investigated using some Cu(II) salts as the precursors in the Cu(II)–PVP (Fig. 8). The turnover number increased with an increase in the ligand ratios, but inversely decreased with a further increase in the ligand ratio, thus passing through a maximum, irrespective of the Cu(II) precursors used in this study. Figure 9 illustrates the effect of the ligand ratio of Cu(II)–poly(4-vinylpyridine-co-styrene) (styrene content, 10%), in the place of PVP. The turnover number for Cu(II)–PVP-co-styrene was found to be appreciably higher than the one for the Cu(II)–PVP catalyst, though both the dependence of the TON on the ligand ratio were almost similar to each other.

Kinetics of BOH oxidation catalyzed by the Cu(II)–PVP in the presence of KOH. The log–log plots of the oxidation rate vs the Cu(II) amount are illustrated by the BOH oxidation catalyzed by the Cu(II)–PVP in the presence of KOH (Fig. 10). To compare the dependence of the Cu(II) amount, the kinetic results based on the homogeneous $CuCl_2$–pyridine catalyst are also shown in Fig. 10. It must be noted that the ligand ratio of the Cu(II)–PVP catalyst varies with the Cu(II) amounts on the PVP, in contrast to the ligand ratio of the homogenous $CuCl_2$–pyridine catalyst, which remained constant. The slope generated by the Cu(II)–PVP catalyst was changed from unity to 2 when the Cu(II) amounts on the Cu(II)–PVP were varied from the higher region to the lower one (the calculated slopes based on the least-squares method were 0.8 and 2.3, respectively). The slope made by the homogeneous $CuCl_2$–pyridine catalyst also had a similar change (the calculated slopes based on the least-squares method were 0.91 and 2.2, respectively). Thus, the oxidation rate was found to be second-order in the Cu(II) amount in the range of the lower amounts of Cu(II) ions (the range of higher ligand ratios) and first-

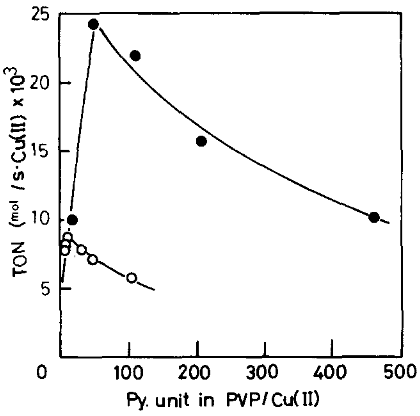


FIG. 9. Influence of the polymer support on the reaction rate: BOH, 5.0 × 10^{-2} *M*; Cu(II)–PVP ($CuCl_2$ used as source of Cu(II) ions), 0.25 g; mole ratio of KOH in the reaction solution to Cu(II), 2.5; solvent, CH_3OH (35 cm^3) + $CHCl_3$(15 cm^3); temp., 303 K; ○, poly(4-vinylpyridine) support; ●, poly(4-vinylpyridine-co-stylene) (styrene content, 10%).

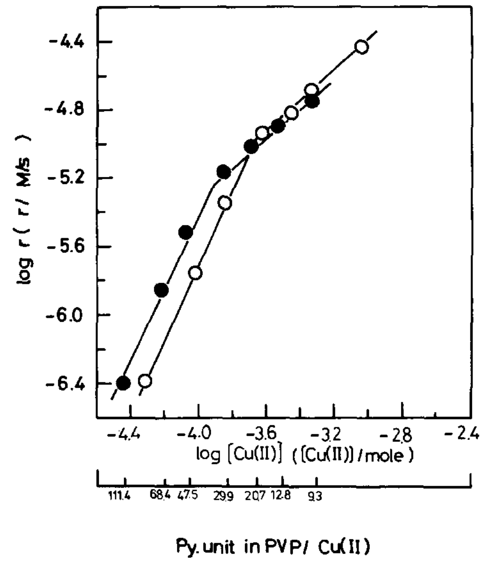


FIG. 10. Log–log plot of the reaction rate vs mole number of Cu(II) ions: BOH, 5.0 × 10^{-2} M; solvent, CH_3OH(35 cm^3) + $CHCl_3$(15 cm^3); temp., 303 K; ●, heterogeneous Cu(II)–PVP catalyst, 0.4525 g; KOH in the reaction solution/Cu(II) = 5.0; ○, homogeneous Cu(II)–pyridine catalyst, pyridine/Cu(II) = 4; KOH/Cu(II) = 1.0.

order in the respect to the Cu(II) amount in the region of the higher amounts of Cu(II) ion (the range of lower ligand ratios), irrespective of the catalytic system of the heterogeneous Cu(II)–PVP or the homogeneous Cu(II)–pyridine. It may be noted that the first-order region for the Cu(II) amount of the Cu(II)–PVP catalyst shifts to the lower Cu(II) amounts, in comparison to the one for the homogeneous Cu(II)–pyridine catalyst.

The log–log plots between the oxidation rate and the amount of the Cu(II)–PVP is illustrated in Fig. 11, in which two Cu(II)–PVP catalysts having the ligand ratios of 9 and 48 were used. The slopes of the straight lines obtained due to catalysis by the Cu(II)–PVP having the ligand ratios of 9 and 48 were found to be unity and 2, respectively (the calculated values based on a least-squares method were 1.0 and 1.9, respectively). Thus, it was confirmed that the rate was first order for the Cu(II) amount using the Cu(II)–PVP catalyst having low ligand ratios and second order for the Cu(II) amount using the Cu(II)–PVP having high ligand ratios which agreed with the results in Fig. 10.

Figure 12 illustrates the relationship between the rate and the partial pressure of oxygen using two Cu(II)–PVP catalysts having the ligand ratios of 9.2 and 65. The rate was found to change from first-order for the partial pressure of oxygen to zero-order with an increase in the partial pressure of oxygen in the case of the Cu(II)–PVP catalyst having the ligand ratio of 9.2. On the other hand, using the Cu(II)–PVP catalyst having the ligand ratio of 65, the rate was first-order for the partial pressure of oxygen in the region of the partial pressures of oxygen investigated in this study. A similar relationship between the rate and the partial pressure of oxygen was obtained in the homogeneous $CuCl_2$–pyridine catalytic systems.

The dependence of the rate on the concentration of BOH is illustrated in Fig. 13

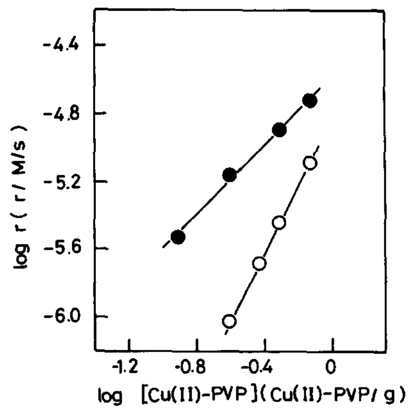


FIG. 11. Log–log plot of the reaction rate vs the weight of the Cu(II)–PVP: BOH, 5.0 × 10^{-2} M; KOH in the reaction solution/Cu(II) = 5, solvent, CH_3OH (35 cm^3) + $CHCl_3$(15 cm^3); temp., 303 K; ●, pyridine unit in PVP/Cu(II) = 9; ○, pyridine unit in PVP/Cu(II) = 48.

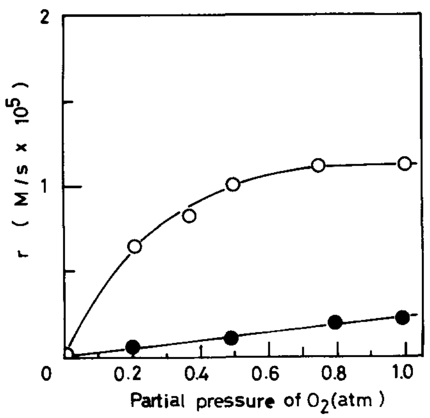


FIG. 12. Plot of the reaction rate vs partial pressure of O_2: BOH, 5.0×10^{-2} *M*; solvent, CH_3OH(35 cm^3) + $CHCl_3$(15 cm^3); ○, KOH in the reaction solution = 4.83×10^{-2} *M*, Cu(II)–PVP (pyridine unit in PVP/Cu(II) = 9.2), 0.5 g; ●, KOH in the reaction solution = 7.24×10^{-3} *M*, Cu(II)–PVP (pyridine unit in PVP/Cu(II) = 65), 0.50 g.

using the two Cu(II)–PVP catalysts in which the rate was first- and second-order for the amount of Cu(II) ions, respectively. The rate due to catalysis by the Cu(II)–PVP having the ligand ratio of 13 was first-order (the slope based on a least-square method was 1.08) in the BOH concentrations in the region of the lower BOH concentrations, but the rates due to catalysis by the Cu(II)–PVP having the ligand ratio of 58 were almost independent on the BOH concentration even in the region of the comparatively lower BOH concentrations.

Re-use of the Cu(II)–PVP and KOH_{imp}*–Cu(II)–PVP catalysts in the oxidation of BOH.* The oxidation of BOH was performed using a fresh and used Cu(II)–PVP and the corresponding KOH_{imp}–Cu(II)–PVP catalyst in order to investigate the possibility of the re-use of these catalysts. The oxidation rates of BOH catalysed by the fresh and used Cu(II)–PVP (BOH, 5.0×10^{-2} *M;* solvent, CH_3OH (35 ml) + $CHCl_3$(15 ml); Cu(II)–PVP (9.9×10^{-4} Cu(II) eq/g-cat, pyridine units in PVP/Cu(II) = 9), 0.25 g; KOH added in the reaction mixture, 1.78×10^{-2} *M* (added KOH/Cu(II) = 3.8); reaction temperature, 303 K) were 6.4×10^{-6} and 6.2×10^{-6} *M*/s, respectively, where the used catalyst was the Cu(II)–PVP catalyst isolated after the oxidation of BOH catalyzed by the fresh Cu(II)–PVP and washed with the mixed solvent of methanol and chloroform. The oxidation rate of BOH catalyzed by a fresh and used KOH_{imp}–Cu(II)–PVP catalysts (11×10^{-4} K^+_{imp} eq/g-cat, KOH_{imp}/Cu(II) = 1) using the same reaction conditions as the Cu(II)–PVP catalysts previously described, except that the KOH added in the reaction mixture was 1.34×10^{-2} *M*, were 8.1×10^{-6} and 6.2×10^{-6} *M*/s, respectively.

Figures 14a and 14b illustrate the relationship between the amount of oxygen absorption and the reaction time in the cases of the consecutive supply of BOH reactant. In Fig. 14a (the KOH/BOH mole ratio of 1.1), after 3 h at which time the amount of oxygen absorption leveled off, BOH (1.6×10^{-2} *M*) was again added to the reaction mixture with and without KOH addition in the reaction solution (sec-

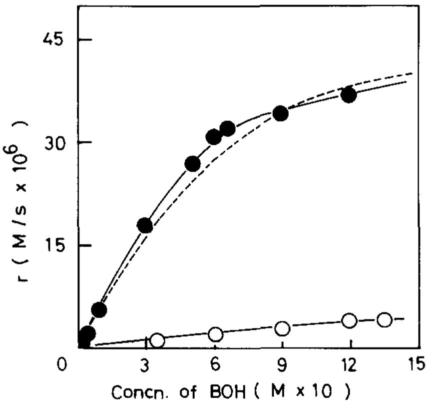


FIG. 13. Plot of the reaction rate vs the concentration of BOH: Cu(II)–PVP, 0.25 g; solvent, CH_3OH(35 cm^3) + $CHCl_3$(15 cm^3); temp., 303 K; ○, pyridine unit in PVP/Cu(II) = 13, KOH in the reaction solution = 8.9×10^{-3} *M*, KOH/Cu(II) = 2.5; ●, pyridine unit in PVP/Cu(II) = 58, KOH in the reaction solution = 4.1×10^{-3} *M*, KOH/Cu(II) = 5; ———, calculated amount (see text).

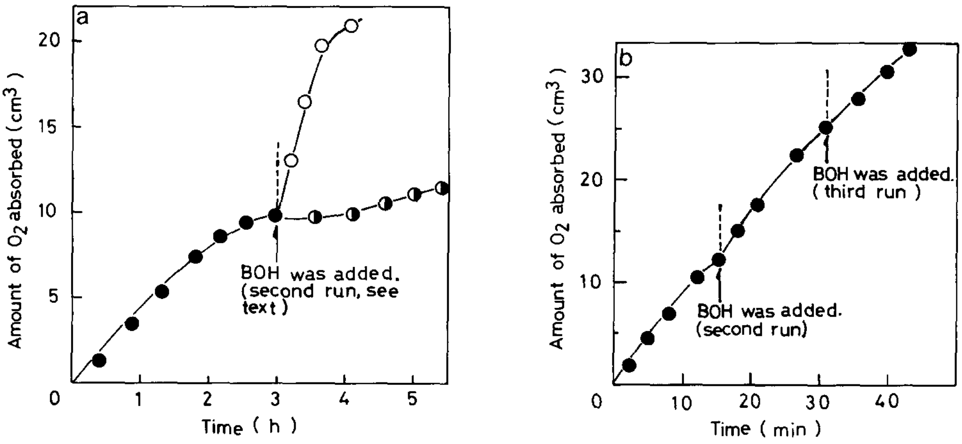


FIG. 14. Plot of absorbed O_2 and reaction time: BOH, 1.6×10^{-2} *M*; Cu(II)–PVP (pyridine unit in PVP/Cu(II) = 9.0), 0.20 g; solvent, CH_3OH(35 cm^3) + $CHCl_3$(15 cm^3); temp., 303 K: (a) KOH in the reaction solution, 1.78×10^{-2}*M*; KOH/Cu(II) = 1.1; ●, first run; ○, second run, KOH (1.78×10^{-2} *M*) addition to the reaction solution; ◑, second run, no KOH addition to the reaction solution. (b) KOH in the reaction solution, 8.1×10^{-2} *M*; KOH/Cu(II) = 5; 1.6×10^{-2} *M* of BOH was added to the second and third runs.

ond run). With KOH (1.78×10^{-2} *M*) addition, the oxygen uptake was observed at the rather higher rate than that of the first run. On the other hand, the rate of the oxygen uptake without KOH addition was appreciably lower than that of the first run. In the case of the high KOH/BOH mole ratio of 5 (Fig. 14b), the continuous use of the Cu(II)–PVP catalyst has tried without KOH addition in the reaction mixture. It is evident that both the BOH (1.6×10^{-2} *M*) additions (second and third runs in Fig. 14b) cause the uptake of oxygen at rates similar to the one from the first run. Thus, Cu(II)–PVP catalyst was found possible to be reused, if excess KOH was present in the reaction mixture for the BOH oxidation with oxygen.

DISCUSSION

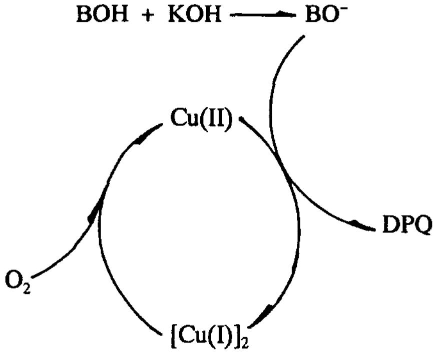
Cu(II)–PVP catalyst in the oxidation of 2,6-di-tert-butylphenol. It was found that only the Cu(II)–PVP itself had no catalytic activity during the oxidation of BOH, but the presence of a base like KOH could catalyze the BOH oxidation (*18, 19, 25, 26*). The corresponding potassium phenolate can be oxidized even by using the Cu(II)–PVP without KOH and an almost similar yield as that obtained in the BOH oxidation catalyzed by the Cu(II)–PVP with KOH in the reaction solution was attained (Table 1). The role of the base such as KOH was thus to interact with the BOH molecule to form the corresponding phenolate salt, which is known to be more oxidizable than the original phenol because of the difference between their redox potentials (*27*). The KOH in the reaction solution has been considerably more effective during the BOH oxidation than the KOH directly impregnated in the Cu(II)–PVP catalyst, though the KOH_{imp}–Cu(II)–PVP catalyst had appreciably higher catalytic activity in the BOH oxidation than the Cu(II)–PVP itself without KOH (Fig. 6). The excess impregnated amount of KOH in the Cu(II)–PVP caused a sharp decrease in the oxidation activity and the oxidation activity became lower than that of the Cu(II)–PVP without the impregnated KOH, in spite of the presence of KOH in the reaction solution (Fig. 6). This may suggest that the excess of the impregnated KOH in the Cu(II)–PVP catalyst retards access of the BOH molecules to the Cu(II) in the PVP support since the coordination sphere of Cu(II) ions have been already saturated with the presence of excess KOH, in addition to the change in the charge of the Cu ion as described in the RESULTS section.

There is the alternative to the stoichiometry of the BOH oxidation to DPQ which is shown in Eq. (1) or Eq. (2). Since both the amounts of oxygen uptake and formed diphnoquinone (DPQ) were almost identical at each reaction time and the accumulation of H_2O_2 formed was less than 10% of the formed DOP, it is reasonable to consider that the main stoichiometry of the BOH oxidation is Eq. (1), in which the accumulation of hydrogen peroxide is not observed, rather than Eq. (2). The stoichiometry of 3,5-di-*tert*-butylcatechol to the corresponding *ortho*-benzoquinone catalyzed by the homogeneous Cu(II) chelate and the heterogeneous Cu(II)–PVP was also the one which did not accumulate any hydrogen peroxide (*13*).

The kind of Cu(II) salt and/or its chelate complex supported in the PVP polymer were found to appreciably affect the turnover number of the Cu(II)–PVP catalyst in the BOH oxidation (Table 2). The turnover numbers of the simple Cu(II) salts such as $CuCl_2$ supported on the PVP were found to be comparatively small and were similar values but the Cu(II) chelate precursors have tended to make the turnover numbers diversify. The Cu(II) chelates in which the Cu(II) ion was coordinated with oxygen atoms rather than nitrogen atoms have thus tended to have larger turnover numbers. The similar trend in the oxidation activity (the turnover number) of the Cu(II) chelates already mentioned has been previously reported for the oxidation of 3,5-di-*tert*-butylcatechol catalyzed by homogeneous Cu(II) chelates and/or heterogeneous Cu(II)–PVP systems (*13*), and also in the oxidations of 2,6-dimethylphenol and 2,6-di-*tert*-butylphenol catalyzed by Cu(II) chelates–amine complexes (*28*). These differences in the oxidation activity of the Cu(II) chelates may be related to the stability of the corresponding Cu(II) chelate as has been previously suggested (*33*): the stability of the Cu(II) chelates, which were coordinated with four nitrogen atoms, were too high to access a reactant in comparison with the Cu(II) chelates in which the Cu(II) was coordinated with oxygen atoms.

The effect of the ligand ratio on the turnover number of the Cu(II)–PVP catalyst was investigated using various Cu(II) precursors as illustrated in Fig. 8. One identified feature was that the turnover number of the catalysts had a maximum value, irrespective of the Cu(II) precursors used here. This suggests that the optimum oxidation activity is obtained using the Cu(II)–PVP catalyst with the unsaturated coordination number. A similar behavior in the relationship between the turnover number and the ligand ratio has been observed for the oxidation of 3,5-di-*tert*-butylcatechol to the corresponding *ortho*-benzoquinone catalyzed by the Cu(II)–PVP system (*13*).

Mechanistic scheme of the phenol oxidation. The log–log plots between the initial rate and the amount of Cu(II) ions were obtained as folded linear lines, irrespective of the heterogeneous Cu(II)–PVP and/or homogeneous Cu(II)–pyridine catalytic systems, as shown in Fig. 10. The initial rate was thus second order in the amount of the Cu(II) ions in the region of the lower Cu(II) amounts and was first order with respect to the amount of the Cu(II) ions in the region of the higher amount of the Cu(II) ions. Speier (*29*) has kinetically studied the oxidation of catechol derivatives catalyzed by chloro(pyridine) Cu(II) complexes. The rate-determining step of the catechol oxidation was assumed to be the formation step of dinuclear Cu species resulting from the reaction between the mononuclear Cu–oxygen adduct and CuCl(pyridine) on the basis of the results that the overall rate equation showed second-order in the catalyst, first-order in the oxygen molecule, and zero-order in the catechol concentrations. We have also studied (*30*) the oxidation of 3,5-di-*tert*-butylcatechol catalyzed by Cu(II) chelate–pyridine complexes. The kinetic investigation of this oxidation reaction showed that the formation rate of *ortho*-benzoquinone was second-order in the catalyst and zero-order in the catechol concentrations. From the kinetic results, and the stoichiometric and electronic absorption results, we have proposed a reaction scheme in which dimeric Cu species act as the active catalytic species for the catechol oxidation. A mechanistic study of the oxidation of 2,6-dimethylphenol by 4-(N,N-dimethylamino)pyridine (DMAP) and polystyrene-bound DMPA-based Cu catalysts has been studied by Challa *et al.* (*31*). It has been concluded (*31*) that the dimerization of Cu(I) complexes is needed to allow for the reoxidation step of Cu(I), from the difference in the reaction order in Cu for the phenol oxidation and the Cu(I) dimerization, namely, first- and second-order, respectively. Thus, the study showed that for a low molar mass catalyst, the dimerization reaction of Cu(I) species is rate-limiting, and for a high molar mass catalyst the phenol oxidation step, in which the mononuclear Cu(II) species catalyze the phenol (or the corresponding phenolate anion) oxidation, is the rate-determining step. Based on the mechanistic aspects of the Cu species in the phenol oxidation previously described and the kinetic results obtained in this study, some key information concerning the function of the Cu species in the phenol oxidation studied here can be deduced. In the region of higher Cu(II) amounts of both the Cu(II)–PVP and the Cu(II)–pyridine catalytic systems, the oxidation of the phenol with mononuclear Cu(II) species was assumed to be the rate-determining step. The rate was found to be first-order with respect to the concentration of BOH (Fig. 13) and zero-order (at one atmosphere in Fig. 12) for the partial pressure of oxygen molecule in the region of the lower ligand ratios, in other words, in the first-order region in the Cu(II) amount. These kinetic results are consistent with the assumption that the rate-determining step is the phenol oxidation with mononuclear Cu(II) species. In the region of the higher ligand ratios (the region of the lower Cu(II) amount) in which the rate was second-order in the Cu(II) amount (Figs. 10, 11), the rate was first-order for the partial pressure of the oxygen molecule (Fig. 12). The reoxidation step of the dimeric Cu(I) species by oxygen molecules in the region of the lower Cu(II) amount is considered as the rate-determining step. The dependence of the rate on the BOH concentration in the region of lower Cu(II) amounts was found to be considerably smaller than unity (0.39 order based on the least-squares method), though the rate was not zero-order in the BOH concentration, as expected from the assumed rate-determining step. The rate-determining step in the BOH oxidation catalyzed by the Cu(II)–PVP with KOH in the reaction solution was thus suggested to change from the reoxidation of dinuclear Cu(I) by an oxygen molecule to the oxidation of the phenol by mononuclear Cu(II) with an increase in Cu(II) amount in the Cu(II)–PVP catalyst, pointed out previously by Challa *et al.* (*31*). The kinetic results obtained in the BOH oxidation catalyzed by the homogeneous Cu(II)–pyridine complex were similar to those in the Cu(II)–PVP catalyst. The mechanistic feature of the heterogeneous Cu(II)–PVP catalyst previously described will be applied to the homogenous Cu(II)–pyridine catalyst. However, the difference in both the catalytic systems may be noted, thus, the folded region of the Cu(II)–PVP catalystic system in the linear relationship between log r and log [Cu(II)] in Fig. 10 shifted to the region of the lower Cu(II) amounts in comparison with the one for the homogeneous Cu(II)–pyridine catalyst. These results will be due to the fact that the localized concentration of the Cu(II) ions in the PVP support is higher than the concentration of the homogeneous Cu(II)–pyridine, since the Cu(II) ions are locally anchored on the PVP polymer support. A plausible scheme for the oxidation of BOH catalyzed by the Cu(II)–PVP system is illustrated as follows:



Reaction Scheme

To investigate whether the kinetics of the Michaelis–Menten type can be applied to the BOH oxidation catalyzed by the Cu(II)–PVP with KOH in the reaction solution under the reaction condition of the rate-determining step being the BOH oxidation by the mononuclear Cu(II), the relationship between the reciprocal of the rate (r^{-1}) vs the reciprocal of the BOH concentration ($[BOH]^{-1}$) was plotted using the reaction temperature (293, 298, 303, 308 K; KOH/Cu(II) = 5 and also 303 K; KOH/Cu(II) = 2.5) as a parameter, and straight lines intersecting the y-axis were confirmed according to

$$1/r = 1/(k[KOH][Cu(II)\text{–}PVP]) + K/(k[KOH][Cu(II)\text{–}PVP])\ 1/[BOH].$$

From the slope and the intersection of these straight lines, the k (rate constant) and K Michaelis-Menten constant) were obtained with the results in Table 3. The plots between the rates at 303 K calculated using the obtained k and K vs. Cu(II)–PVP amount and the concentration of BOH are illustrated as dotted lines in Figs. 5 and 13, respectively, and are in good agreement with the experimental results. The apparent activation energy for BOH oxidation catalyzed by the Cu(II)–PVP system (KOH/Cu(II) = 5) in the temperature range of 293–308 K was calculated to be 92 kJ/mol (prefrequency factor: 2.0×10^{-2} s^{-1} g-cat^{-1}) from the slope of the straight line of the Arrhenius plots.

CONCLUSION

The oxidation of 2,6-di-*tert*-butylphenol (BOH) catalyzed by Cu(II)–PVP with an inorganic base such as KOH under a variety of reaction conditions was investigated to shed light on the reaction scheme. The only product was 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone. The addition of inorganic base caused similar rates in the BOH oxidation, regardless of the kind of the inorganic base used in this study. The mixed solvent of $CH_3OH/CHCl_3$ = 7/3 vol% had the maximum activity for the oxidation of BOH (Fig. 2). The maximum rate of the BOH oxidation was obtained at a KOH/Cu(II) mole ratio of ca. 5, irrespective of the KOH concentration. The kind of Cu(II) salts and/or its chelate complex supported in the PVP polymer were found to appreciably affect the oxidation activity of the Cu(II)–PVP in the BOH oxidation (Table 2). The role of KOH was found to dissociate the phenol to form the corresponding phenolate which is more easily oxidized. From the kinetic results, the rate-determining step was found to be a shift

TABLE 3

Kinetic Parameters in the Cu(II)–PVP Catalytic System[a]

KOH/cu(II) mole ratio	Reaction temp. (K)	k (s^{-1} g-cat^{-1} $\times 10^2$)	K^{-1} (mol^{-1})
2.5	303	3.3	0.87
	293	0.78	3.3
5.0	298	1.4	2.1
	303	2.2	1.3
	308	5.3	1.1

[a] Cu(II)–PVP, 0.25 g; pyridine group in PVP/Cu(II) mole ratio, 10; KOH, 8.9×10^{-3} M (KOH/Cu(II) = 2.5), 1.78×10^{-2} M (KOH/Cu(II) = 5); solvent, CH_3OH(35 cm^3) + $CHCl_3$(15 cm^3).

from the BOH oxidation with mononuclear Cu(II) species to the reoxidation step of dimeric Cu(I) with oxygen with a decrease in the Cu(II) amount anchored in the Cu(II)–PVP catalyst.

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