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Homogeneous Copper(II) Chelates and Heterogeneous Cu(II)-Poly(vinylpyridine) Complexes as Catalysts for 3,5-Di-*tert*-butylcatechol Oxidation

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Liquid-phase oxidation of 3,5-di-*tert*-butylcatechol (3,5-DtBC) by molecular oxygen was carried out in the presence of homogeneous Cu(II) chelates or heterogeneous Cu(II)–poly(4-vinylpyridine) (Cu(II)–PVP) catalytic systems. The oxidation product in both cases is 3,5-di-*tert*-butyl-*o*-benzoquinone (3,5-DtBQ). The catalytic activity of the oxidation of 3,5-DtBC catalyzed by the homogeneous Cu(II) system was found to be affected by the Cu(II) chelates used as the catalyst, the addition of pyridine derivatives, and their amounts added. The oxidation activity was found to increase with the basicity of the added pyridine derivatives. The kinetic data obtained from the formation rate of 3,5-DtBQ by the homogeneous bis(acetylacetonato)Cu(II)–pyridine catalytic system showed that the rate was independent of the 3,5-DtBC concentration, second order in the concentration of the catalyst, and first order with respect to the partial pressure of oxygen. The homogeneous copper(II) chelate-catalyzed oxidation of 3,5-DtBC confirmed the stoichiometric equation 3,5-DtBC + $\frac{1}{2}O_2$ = 3,5-DtBQ + H_2O. On the basis of these data, possible mechanistic interpretations are discussed, in which a dimeric Cu(II) complex is assumed to be the active species. The kinetics of 3,5-DtBC oxidation by molecular oxygen in the presence of the heterogeneous Cu(II)–PVP catalyst revealed that both the oxygen absorption rate and effectiveness factor decreased with increasing particle size of the Cu(II)–PVP catalyst. The increase of the particle size of the catalyst was found to cause an increase in the fraction of mass transfer resistance in the total (mass transfer + reaction) resistance of the oxidation reaction.

INTRODUCTION

There have been a wide variety of studies on liquid-phase oxidation catalyzed by transition metal ions and/or transition metal complexes (*1–4*). Usually, transition metal catalysts have been used in a homogeneous form, which is found to be more active and more selective than the heterogeneous catalysts (*5, 6*). Nevertheless, homogeneous catalysts have disadvantages, particularly in separation and recovery from the reaction products. This major disadvantage can be minimized if a well-defined catalytic species is either deposited or chemically bound to an inorganic carrier material or an organic polymer (*7–14*). These catalysts are considered as "heterogenized-homogeneous" catalysts (*15, 16*).

In this paper we present the results of our studies of the catalytic oxidation of 3,5-di-*tert*-butylcatechol (3,5-DtBC) to the corresponding *o*-benzoquinone by a homogeneous copper(II) complex system or by a heterogeneous poly(4-vinylpyridine)–Cu(II) system. The transition metal-catalyzed oxidation of catechol and its derivatives have been the subject of considerable interest for many years because of its synthetic utility and relevance to biological systems (*30–51*).

EXPERIMENTAL

General. IR, UV, and ^{1}H NMR spectra were recorded with a Hitachi Model EPIG-2 spectrophotometer, a Shimazu UV-240 spectrophotometer, and a JEOL Model PS-100 spectrometer, respectively. Gas chro-

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matograms were recorded with a Shimazu Model GC-6A gas chromatograph operating in the flame ionization mode, using all glass column systems (2 m × 3 mm, 10% Silicone SE-30 on Uniport B, 473 K, N_2 20 ml/min). The elementary analyses of the reaction products and copper(II) chelates synthesized as catalysts were performed by the Microanalysis Center, Kyoto University.

Materials. 3,5-Di-*tert*-butylcatechol from Nakarai Chemical Co. was recrystallized from *n*-hexane. Chloroform, pyridine, and methanol from Nakarai Chemical Co. were purified by usual distillations. 4-Cyanopyridine, γ-picoline, and 4-aminopyridine from Nakarai Chemical Co. were used without further purification. Poly(4-vinylpyridine) (PVP) bead (LX-1) as a support was obtained from Mitsubishi Shoji Co. Some chemical and physical properties of the PVP granular solid were as follows: bulk density, 0.45 g/cm^3; skeletal density, 1.154 g/cm^3; apparent pK_a, 5.8; temperature stability, 373 K.

Catalyst preparation. Bis(acetylacetonato)copper(II) ($Cu(acac)_2$) (*17*), bis(salycylaldehydato)copper(II) ($Cu(salad)_2$) (*18*), bis(dimethyglyoximato)copper(II) ($Cu(dmg)_2$) (*19*), and *N*,*N*′-bis(1-methyl-3-oxobutylideneethylenediaminatocopper (II) (Cu(acacen)) (*19*) were prepared by conventional methods. The copper(II) chelates were identified by their mp and elemental analyses. Poly(4-vinylpyridine) beads (LX-1) were sieved to obtain the four groups of the beads of 20–60 mesh (250–840 μm, $\bar{d}_p$ = 545 μm), 60–100 mesh (149–250 μm, $\bar{d}_p$ = 200 μm), 100–200 mesh (74–149 μm, $\bar{d}_p$ = 112 μm), and <200 mesh (0–74 μm, $\bar{d}_p$ = 37 μm). To a suspension (5.0 g) of the sieved poly(4-vinylpyridine) in 50 ml of water was added cupric chloride (0.672 g, 5 mmol). After the solution was stirred for 120 min at 303 K, the solid was filtered and washed with water. The amount of copper(II) ions retained by the polymer was found to be 5.6 × 10^{-4} equivalent Cu(II)/g polymer by iodometry. For the polymer beads with 60–100 mesh, Cu(II)–PVP catalyst with 3.1 × 10^{-4} mol Cu(II) equivalent/g polymer was also prepared. The measure of the degree of swelling of the Cu(II)–PVP catalyst (*H*) was defined (*21*) by Eq. (1). The value of *H* in methanol solvent at 303 K was ca. 60% for the Cu(II)–PVP catalyst used in this study, whose value varied little with the change of the particle size of the catalyst.

$$H = \frac{\text{wt. of wet catalyst} - \text{wt. of dry catalyst}}{\text{wt. of wet catalyst}} \times 100 \quad (1)$$

The oxidation procedure. The reaction vessel used in this experiment was a four-neck 50-ml round-bottom flask equipped with a mechanical stirrer, a dropping funnel, a cooler, and a gas inlet. It was maintained in a thermostated water bath at 30°C (303 K). In a typical experiment, the reaction vessel was charged with 40 ml of chloroform, prescribed amount of $Cu(acac)_2$ catalyst (0.026 g, 0.1 mmol) and pyridine (0.396 g, 5 mmol). The catalytic system was stirred under an oxygen atmosphere for 30–60 min. A dropping funnel was charged with a solution of 3,5-DtBC (1.11 g, 5 mmol) in 10 ml of chloroform and the reactant solution was added to the catalytic system. The reaction solution was stirred vigorously for the prescribed time under an oxygen atmosphere (O_2 flow rate, 80 ml/min). Once the reactions were started, aliquots (0.1 ml) were removed and transferred to a capped sample tube for a known time interval. These were then stored in a dry ice–methanol bath for later analysis by GLC. Initial rates were determined by least-squares analysis of 3,5-di-*tert*-butyl-*o*-benzoquinone (3,5-DtBQ) concentration vs time using six to eight points per run. Dark red needle crystals were obtained as the sole oxidation product, irrespective of the Cu(II) catalysts used, which were characterized as 3,5-DtBQ by their mp, elementary analyses, and IR and NMR spectra.

Oxygen absorption measurement. Oxidation absorption measurements were carried out in a usual constant-pressure gas absorption apparatus containing a reaction vessel with a magnetic stirrer connected to a gas buret and a U-tube manometer. The reaction vessel was thermostated at a prescribed temperature (usually 303 K) and was charged with 20 ml of catalytic solution. The reaction vessel was attached to a pressure-equalized dropping funnel to which 5 ml of 3,5-DtBC solution was added. The whole reaction system was saturated with oxygen for 40 to 60 min under vigorous stirring. When equilibrium was obtained, the 3,5-DtBC solution was added to the catalytic solution in the reaction vessel. The oxygen consumption at constant pressure was measured at regular time intervals.

Analytical procedure for hydrogen peroxide. Aliquots of the reaction mixture conducted with a constant-pressure gas absorption apparatus were taken after the solution was quenched with acid to stop the oxidation of 3,5-DtBC. The aliquots were extracted twice with water and the extracted aqueous layer was analyzed by iodometry (*22*).

Electronic absorption spectra of the reaction solution in an in situ cell. A chloroform solution of the copper(II) acetylacetonato–pyridine system was added to a 1 cm × 1 cm quartz cell with a side tube. After the catalytic solution was degassed under vacuum (10^{-3} Torr), the *in situ* cell was sealed off. The degassed catalytic solution in a side tube was placed in the quartz cell in which the prescribed amount of 3,5-DtBC was present. The visible absorption spectra of the reaction solution at 450–900 nm were measured.

RESULTS

Oxidation activity of 3,5-DtBC catalyzed by copper(II) chelate complexes. In a chloroform solution at 303 K under oxygen, 3,5-DtBC (100 m*M*) remains stable; however, the addition of a catalytic amount of Cu(acac)$_2$ (2.0 m*M*) and pyridine (100 m*M*) to this solution leads to rapid oxidation of the catechol. Under these conditions, the only oxidation product is 3,5-DtBQ. Catalysts Cu(salad)$_2$, Cu(dmg)$_2$, and Cu(acacen) were tried in addition to Cu(acac)$_2$. Cu(salad)$_2$ was approximately as active as Cu(acac)$_2$; however, both Cu(dmg)$_2$ and Cu(acacen) were only about one-fifth as effective as Cu(acac)$_2$ in catalyzing the oxidation of 3,5-DtBC. (Yields after 1 hr based on 3,5-DtBC fed: Cu(acac)$_2$, 82%; Cu(salad)$_2$, 71%; Cu(dmg)$_2$, 16%; Cu(acacen), 17%.) Figure 1 illustrates the time dependence of the yield of 3,5-DtBQ catalyzed by copper(II) chelate–pyridine. As shown by Fig. 1, the absorption of oxygen started immediately after the 3,5-DtBC solution was added to the solutions of Cu(acac)$_2$ and Cu(salad)$_2$, but the oxidation of 3,5-DtBC catalyzed by Cu(dmg)$_2$ or Cu(acacen) had a relatively long induction period. Thus, the oxidation activity of 3,5-DtBC was found to depend mainly on the copper(II) chelate used as a catalyst. The copper(II) chelate in which the copper(II) ion is surrounded by four oxygen atoms of the chelate ligand seems to have higher catalytic activity for 3,5-DtBC oxidation than the copper(II) chelate in which the copper(II) ion is surrounded by two or four nitrogen atoms of the chelate ligand. A similar trend for the catalytic activity of the

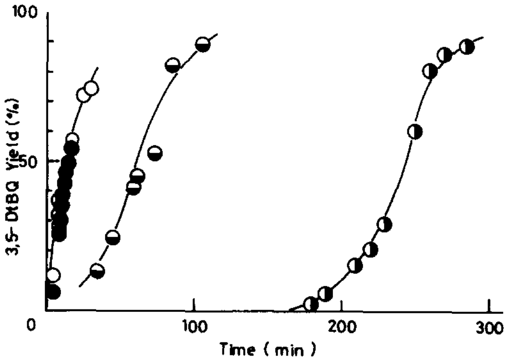
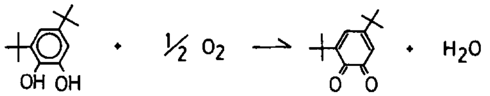


FIG. 1. The dependence of 3,5-DtBQ yield on the reaction time: 3,5-DtBC, 100 m*M*; Cu(II) chelate, 2 m*M*; pyridine, 30 mM; temperature, 303 K; CHCl$_3$, 50 ml; O$_2$ atmosphere; ○, Cu(salad)$_2$; ●, Cu(acac)$_2$; ⊖, Cu(dmg)$_2$; ◑, Cu(acacen).

copper(II) chelate catalysts was observed in the case of the oxidative coupling reaction of 2,6-dimethylphenol (*23*).

Stoichiometry of 3,5-DtBC oxidation catalyzed by copper(II) chelates. The yields of 3,5-DtBQ from the oxidation of 3,5-DtBC are presented in Table 1 for the $Cu(acac)_2$- and $Cu(acac)_2$–pyridine-catalyzed systems. The apparent accumulation of H_2O_2 during oxidation of 3,5-DtBC catalyzed by both Cu(II) catalytic systems was found to be rather small. Also, the total moles of oxygen absorbed during the oxidation was one-half of the number of moles of 3,5-DtBC. Thus, with the $Cu(acac)_2$- or $Cu(acac)_2$–pyridine catalytic systems, the overall stoichiometry of the oxidation of 3,5-DtBC may be represented as follows:



Kinetics of 3,5-DtBC oxidation catalyzed by copper(II) chelates. The kinetics of 3,5-DtBC oxidation were studied by means of the $Cu(acac)_2$–pyridine system as a catalyst. Figure 2 illustrates the relationship between log *r* (where *r* is the formation rate of 3,5-DtBQ) and log O_2, log $Cu(acac)_2$, or log 3,5-DtBC at 303 K. The slope of the linear variation of the log rate with the log partial pressure of oxygen approximates unity (Fig. 2a). Figure 2b shows that the reaction rate is second order with respect to $Cu(acac)_2$ concentration. It was found from Fig. 2c that the oxidation rate was almost independent of the concentration of 3,5-DtBC. From these kinetic results, the rate law for the 3,5-DtBC oxidation catalyzed by $Cu(acac)_2$–pyridine may be given by

$$r = k \cdot [Cu(acac)_2]^2 \cdot [O_2]. \qquad (2)$$

TABLE 1

Stoichiometry of Cu(II) Chelate-Catalyzed Oxidation of 3,5-DtBC[a]

Catalytic system	% O_2[b]	% 3,5-DtBQ[b]	% H_2O_2[c]
$Cu(acac)_2$[d]	100	100	3.8
$Cu(acac)_2$–pyridine[e]	100	100	5.0

[a] Solvent, 20 ml of $CHCl_3$; reaction temp, 303 K; O_2 atmosphere.
[b] Conforms to 3,5-DtBc + $\frac{1}{2}O_2 \rightarrow$ 3,5-DtBQ + H_2O.
[c] Determined by iodometry.
[d] 3,5-DtBC, 100 mM; $Cu(acac)_2$, 2 mM.
[e] 3,5-DtBC, 100 mM; $Cu(acac)_2$, 2 mM; pyridine, 100 mM.

TABLE 2

Kinetic Parameters for 3,5-DtBC Oxidation[a]

Catalyst	T (K)	k ($cm^6/mol^2 \cdot s$)	$\Delta H\ddagger$[b] (kJ/mol)	$\Delta S\ddagger$[b] (J/mol · K)
$Cu(acac)_2$	284	5.53		
	289	6.83		
	293	8.50	13.2	−64.3
	303	8.88		
	313	10.70		
$Cu(salad)_2$	288	6.32		
	293	7.95		
	298	10.00	24.9	−23.9
	303	10.80		
	308	13.60		

[a] Catalyst, 2.0×10^{-6} mol/cm³; pyridine, 3.0×10^{-4} mol/cm³; 3,5-DtBC, 1.0×10^{-4} mol/cm³; solvent, 50 ml of $CHCl_3$; O_2 atmosphere.
[b] Calculated on the assumption that Ostwald solubility parameter (β = 0.217 at 289.3 K) of oxygen in $CHCl_3$ varies according to the variation of the β of oxygen in $CHCl_3$ in temperature.

From Arrhenius plots for the oxidation rate in the temperature ranges of 284 to 313 K and 288 to 308 K, the apparent activation energy for the 3,5-DtBC oxidation was calculated to be 15.7 kJ/mol for the $Cu(acac)_2$ catalyst and 27.4 kJ/mol for the $Cu(salad)_2$ catalyst, respectively (see Table 2). For the $Cu(acac)_2$ catalyst, the rate constant (*k*) was

$$k = 4.60 \times 10^{10} \exp(-15.7/RT) \qquad (284\text{–}313\ \text{K}) \quad (3)$$

and for $Cu(salad)_2$ catalyst

$$k = 6.08 \times 10^{12} \exp(-27.4/RT) \qquad (288\text{–}308\ \text{K}) \quad (4)$$

Effect of substituted pyridines on the catalytic activity of 3,5-DtBC oxidation. The effects of pyridine, 4-cyanopyridine, γ-picoline, and 4-aminopyridine are illustrated in Fig. 3. The rate of oxygen absorption increased at first with the addition of pyridine derivatives and leveled off with the addition of more pyridine derivatives. An excess of the pyridine derivatives was found to cause deactivation of the Cu-

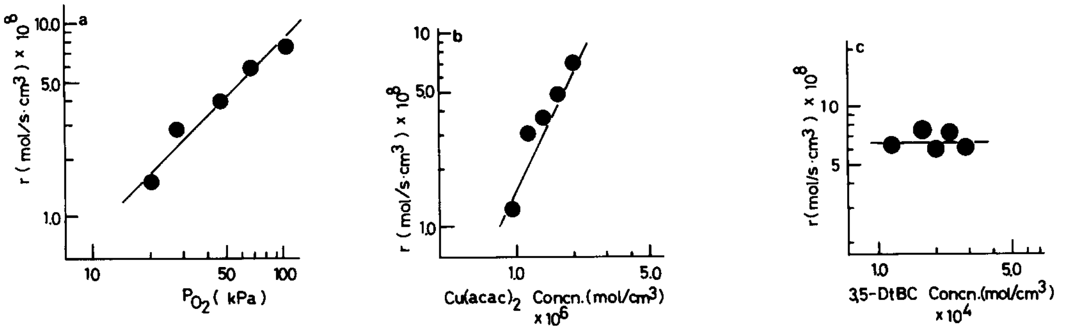


FIG. 2. Log–log plots of the 3,5-DtBQ production rate vs the partial pressure of O_2 and the concentrations of $Cu(acac)_2$ and 3,5-DtBC: (a) 3,5-DtBC, 100 m*M*; $CHCl_3$, 50 ml; pyridine, 100 m*M*; temperature, 303 K; (b) 3,5-DtBC, 100 m*M*; $CHCl_3$, 50 ml; temperature, 303 K; (c) $Cu(acac)_2$, 2 m*M*; pyridine, 30 m*M*; $CHCl_3$, 50 ml; temperature, 303 K.

$(acac)_2$ catalyst. Figure 4 illustrates the relationship between log *k* and pK_a (the K_a of the protonated conjugate acid of the pyridine derivatives) in the series of pyridine derivatives where *k* is the rate constant of the maximum rate in Fig. 3. It is evident from Fig. 4 that the catalytic activity for 3,5-DtBC oxidation increases with an increase of the pK_a value of the added pyridine derivative and thus increases with increasing basicity.

3,5-DtBC oxidation with the Cu(acac)₂–pyridine system under a nitrogen atmosphere. The reaction of 3,5-DtBC with the $Cu(acac)_2$–pyridine system was performed under a nitrogen atmosphere, where Cu $(acac)_2$ was used as an oxidant rather than as a catalyst (reaction condition: 3,5-DtBC, 100 m*M*; $Cu(acac)_2$, 50 m*M*; pyridine, 100 m*M*; solvent, $CHCl_3$; temperature, 303 K; under a nitrogen atmosphere). 3,5-DtBQ was found to be formed in the yield of ca. 12% after 2 hr by quantitative analysis by an electronic absorption spectrophotometer. Figure 5 illustrates the visible absorption spectra of the reaction solutions in the absence of oxygen. It is apparent that during the conversion of 3,5-DtBC to 3,5-DtBQ with $Cu(acac)_2$, the concentration of the Cu(II) ion was decreasing in the absence of oxygen. Thus, the $Cu(acac)_2$ was found to act, in this case, as an oxidant for 3,5-DtBC oxidation.

3,5-DtBC oxidation catalyzed by hetero-

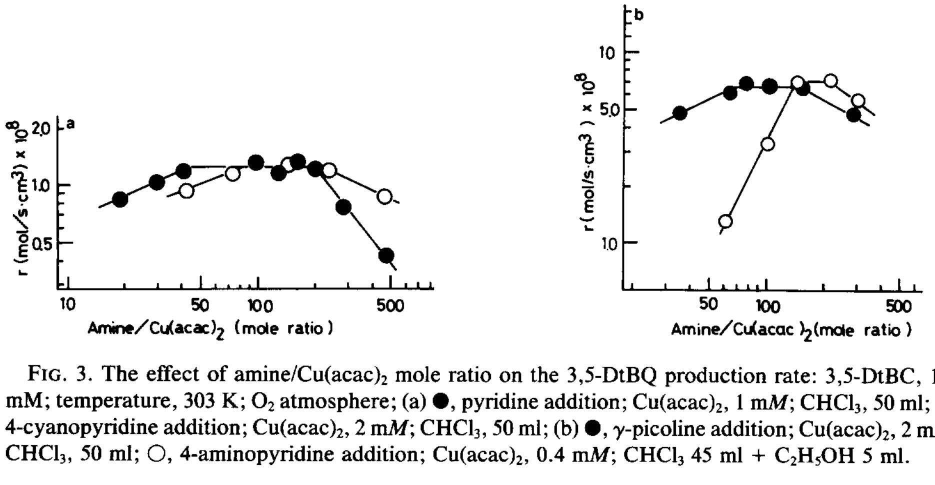


FIG. 3. The effect of amine/$Cu(acac)_2$ mole ratio on the 3,5-DtBQ production rate: 3,5-DtBC, 100 mM; temperature, 303 K; O_2 atmosphere; (a) ●, pyridine addition; $Cu(acac)_2$, 1 m*M*; $CHCl_3$, 50 ml; ○, 4-cyanopyridine addition; $Cu(acac)_2$, 2 m*M*; $CHCl_3$, 50 ml; (b) ●, γ-picoline addition; $Cu(acac)_2$, 2 m*M*; $CHCl_3$, 50 ml; ○, 4-aminopyridine addition; $Cu(acac)_2$, 0.4 m*M*; $CHCl_3$ 45 ml + C_2H_5OH 5 ml.

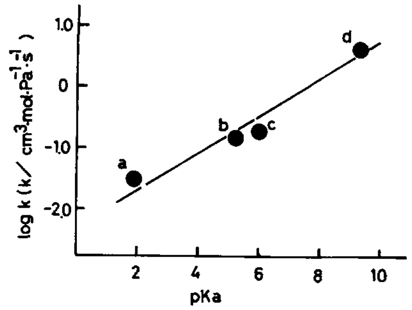


FIG. 4. Relationship between log k and pK_a: (a) 4-cyanopyridine; (b) pyridine; (c) γ-picoline; (d) 4-aminopyridine.

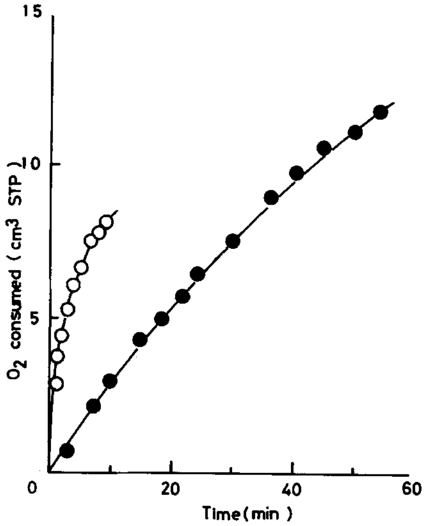


FIG. 6. Time dependence of the amount of O_2 absorption: 3,5-DtBC, 30 mM; CH_3OH, 25 ml; temperature, 303 K; 600 rpm; O_2 atmosphere ●, Cu(II)–PVP, 1.0 g (Cu content, 5.6 × 10^{-1} mmol/g PVP); ○, $Cu(acac)_2$, 100 mM; pyridine, 15 mM.

geneous Cu(II)–poly(4-vinylpyridine). The time dependence of oxygen absorption in 3,5-DtBC oxidation catalyzed by the Cu(II)–poly(4-vinylpyridine) complex (Cu (II)–PVP) is illustrated in Fig. 6, together with that of 3,5-DtBC catalyzed by the homogeneous $Cu(acac)_2$–pyridine complex system. It is evident that the initial rate in the homogeneous $Cu(acac)_2$ catalyst is faster than the rate of the heterogeneous Cu(II)–PVP catalytic system. Thus, the initial rate of oxygen absorption per Cu(II) ion in the heterogeneous Cu(II)–PVP catalyst was about one-tenth of that of the homogeneous $Cu(acac)_2$–pyridine catalyst. However, the rate of oxygen absorption with the homogeneous $Cu(acac)_2$ catalyst seems to have a tendency to decrease faster with reaction time than with the heterogeneous Cu(II)–PVP catalyst. Thus, the homogeneous copper(II) chelate catalytic system considerably deactivated 3,5-DtBC oxidation with reaction time.

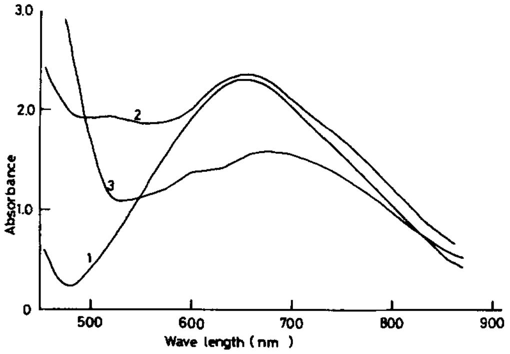


FIG. 5. Electronic absorption spectra of the reaction solution: 1, $Cu(acac)_2$, 40 mM; pyridine, 400 mM; $CHCl_3$, 4 ml; under air; 2, 3, 3,5-DtBC, 40 mM; $Cu(acac)_2$, 40 mM; pyridine, 40 mM; $CHCl_3$, 4 ml; degassed in *in situ* cell; 2, initial stage; 3, after 12 hr.

The oxidation rate was almost independent of the stirring rate at more than ca. 200 rev/min, irrespective of the diameters of the catalyst particle, indicating that the resistance to the transport of oxygen from the gas phase to the heterogeneous solid catalyst is negligible above 200 rev/min. All subsequent rate measurements were made at 600 rev/min.

The effect of Cu(II) ion supported on PVP particle. To investigate the effect of the supported Cu(II) ions, two kinds of Cu(II)–PVP catalysts were prepared with 5.6 × 10^{-4} and 3.1 × 10^{-4} mol of Cu(II) equivalent. Figure 7 illustrates the time dependence of the amount of oxygen absorption catalyzed by the Cu(II)–PVP systems. It is evident that the increase of Cu(II) ion supported on the PVP particle caused the increase of the catalytic activity

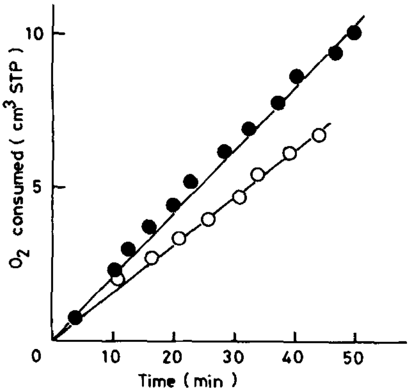


FIG. 7. Influence of Cu(II) ions supported in PVP on the amount of O_2 absorbed: catalyst, 1.0 g (37 μm); 3,5-DtBC, 30 m*M*; temperature, 303 K; CH_3OH, 25 ml; 600 rpm; O_2 atmosphere; Cu content (mmol/g PVP); ●, 0.56; ○, 0.31.

in 3,5-DtBC oxidation. However, it is of interest to note that the rate of oxygen absorption per Cu(II) ion catalyzed by Cu(II)–PVP of 3.1×10^{-4} mol Cu(II) eq/g polymer (1.87×10^{-5} mol/s · cm^3 Cu(II) eq) was larger than that catalyzed by the Cu(II)–PVP of 5.6×10^{-4} mol Cu(II) eq/g polymer (1.12×10^{-5} mol/s · cm^3 Cu(II) eq).

Effect of the concentration of 3,5-DtBC on the Cu(II)–PVP-catalyzed oxidation. The initial rates of oxygen absorption, determined from the slopes of the oxygen consumption plots for the oxidation of 3,5-DtBC, were plotted against 3,5-DtBC concentration, from which results the reaction rate was found to remain unchanged at 3,5-DtBC concentrations beyond ca. 1.0×10^{-4} mol/cm^3.

Kinetic analysis in the Cu(II)–PVP-catalyzed oxidation of 3,5-*DtBC.* The kinetics of olefin hydrogenation in a slurry system have been analyzed well by Satterfield (*24*). The analysis and nomenclature of Satterfield were adopted here and were applied to the Cu(II)–PVP catalyst, with the exception that the diffusion of the gaseous reactant in the swollen polymeric gel occurs not through pores but rather by a process, known as "activated diffusion," in a gel. As has been previously described (*14*), activated diffusion occurs in homogeneous polymers swollen by a solvent, because only extremely small, transient voids exist, and the polymer chains are thermally agitated. The chain movements create small temporary voids adjacent to small, diffusing molecules which move into the voids under the driving force of a concentration gradient to produce a net flux. In line with these analyses, only oxygen transport processes need be considered for the oxidation of 3,5-DtBC. Oxygen must be absorbed from the gas bubbles and be transported through mixing and diffusion of the reaction solution to the catalyst particles on the surface of Cu(II)–PVP. In many instances, the gas side resistance is negligible, and the liquid at the gas–liquid interface is essentially in equilibrium with the gas. This equilibrium concentration of oxygen in the reaction solution will be designated C_i. The bulk body of the reaction solution is at a lower oxygen concentration C_L, and the concentration at the surface of the catalyst particle is C_s. At quasi-steady state, the rate equation may be written as

$$-r_L = k_G a_L (p - p_i) \quad \text{(bulk gas to gas interface)} \tag{5}$$

$$= k_L a_b (C_i - C_L) \quad \text{(gas interface to bulk liquid)} \tag{6}$$

$$= k_p a_s (C_L - C_s) \quad \text{(bulk liquid to particle surface)} \tag{7}$$

$$= k_s a_s C_s \text{ (surface reaction)}, \tag{8}$$

where k_G, k_L, and k_p are mass transfer coefficients (cm/s) and k_s is the first-order rate constant per unit interface area. The rate, $-r_L$, the interface area between gas and liquid, a_b, and the surface area of the solid particle, a_s, are based on a unit volume of liquid. If Henry's law holds,

$$p_i = H_G C_i \tag{9}$$

where H_G is Henry's constant. Combining equations (5), (6), (7), (8), and (9) to eliminate p_i, C_i, and C_s, we have

$$-\frac{C_e}{r_L} = \left(\frac{1}{k_G H_G} + \frac{1}{k_L}\right)\frac{1}{a_L} + \left(\frac{1}{k_p} + \frac{1}{k_p}\right)\frac{1}{a_s} \quad (10)$$

and

$$a_s = \frac{6W}{V\, d_p\, \rho_p}, \quad (11)$$

where $C_e = P/H_G$ (C_e is the equilibrium concentration of O_2 in the bulk liquid corresponding to the partial pressure (P) of the O_2 in the gas bulk), a_s is the surface area of the solid particle per unit volume of liquid, W is the weight of solid particle with density ρ_p in a volume V, and d_p is the diameter of the solid particle, assumed to be spherical. The mass transfer resistance for a gas film, $1/k_G$, may be insignificant, provided that pure gas is used in the reaction. Substituting Eq. (11) in Eq. (10) and assuming $1/k_G \approx 0$, yields Eq. (12).

$$-\frac{1}{r_G V} = \frac{1}{k_L a_L C_e V} + \frac{d_p \rho_p}{6 C_e W}\left(\frac{1}{k_p} + \frac{1}{k_s}\right) \quad (12)$$

Thus in a series of runs varying only catalyst loading, the reciprocal of the rate $-1/r_G V$ should be linear in $1/W$, and the intercept and the slope of the straight line should give the values $1/k_L$ and $1/k_p + 1/k_s$, respectively.

On the other hand, on the assumptions that the mass transfer resistance for gas to liquid is insignificant ($1/k_L \approx 0$) and that the rate of the surface reaction on solid catalyst is comparatively fast, Eq. (12) can be expressed as

$$-\frac{r_G V}{W} = \frac{6 k_p}{d_p \rho_p} C_e. \quad (13)$$

To utilize Eqs. (12) and (13) involving d_p, ρ_p, and W, which refer to a swollen particle, it is necessary to recognize that in actual experiments the corresponding values were known only for the dry particle. The following relations (Eqs. (14), (15), and (16)) adopted by Chanda and his co-workers (*21*) were used for their calculation:

$$W = \frac{w}{1 - (H/100)} \quad (14)$$

(where w is the weight of a dry particle and H is the degree of swelling and is defined by Eq. (1))

$$d_p = \bar{d}_p \left(\frac{1}{1 - (H/100)}\right)^{1/3} \quad (15)$$

$$\rho_p = \left(\frac{H}{100}\left(\frac{1}{\rho_s} - \frac{1}{\rho_p}\right) + \frac{1}{\rho_p}\right)^{-1}, \quad (16)$$

where $\bar{d}_p$ is the average diameter of the dry particles determined by sieve analysis, ρ_s is the density of the liquid medium of the slurry, and ρ_p is the density of the dry catalyst particles.

The plots of $1/(-r_{O_2})V$ vs $1/W$ in terms of Eq. (12) illustrated in Fig. 8 confirm that the resistance to oxygen transport from the gas phase to the slurry is insignificant under the reaction conditions used here. From the slopes of Fig. 8, the value of $(1/k_p + 1/k_s)$ for the various catalyst particle sizes can be calculated.

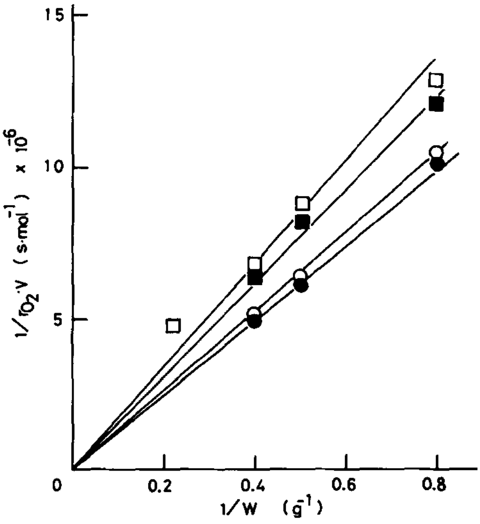


FIG. 8. Plot of reciprocal rate of reaction vs reciprocal weight of Cu(II)–PVP of different particle sizes: 3,5-DtBC, 30 m*M*; temperature, 303 K; CH_3OH, 25 ml; 600 rpm; O_2 atmosphere; □, 545 μm; ■, 200 μm; ○, 112 μm; ●, 37 μm.

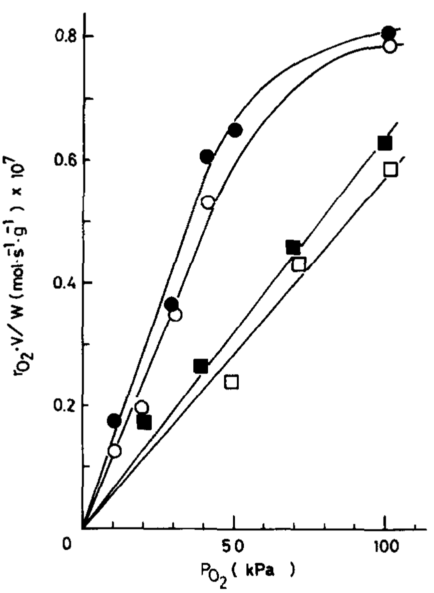


FIG. 9. Plot of reaction rate per unit weight of Cu(II)–PVP vs partial pressure of oxygen for different particle sizes: 3,5-DtBC, 30 m*M*; temperature, 303 K; CH_3OH, 25 ml; 600 rpm; catalyst, 1.0 g; □, 545 μm; ■, 200 μm; ○, 112 μm; ●, 37 μm.

The effect of oxygen partial pressure on the oxygen absorption rate is shown in Fig. 9. It is reasonable to infer from Fig. 9 that the curvature in the plot of oxygen pressure vs rate arises from the mass transfer through the liquid (k_p). This is the rate-controlling process at low oxygen pressures. Thus, Eq. (13) may be applied to the initial portion of Fig. 9 to calculate k_p from the slope. Combining this with the value of $(1/k_p + 1/k_s)$ from Fig. 8 yields the value of k_s. The values of k_p and k_s thus obtained for the different particle size ranges used in this work are shown in Table 3. The surface rate constant obtained, k_s, is only an apparent constant whose value may be greatly influenced by the effective diffusivity of oxygen in the particle, D_e. The importance of this diffusivity can be quantified by the Thiele modules, Φ, and the effectiveness factor, η:

$$\Phi = \frac{R}{3}\sqrt{\frac{k_m \rho_p}{D_e}} \tag{17}$$

$$\eta = \frac{1}{\Phi}\left(\frac{1}{\tanh(3\Phi)} - \frac{1}{3\Phi}\right), \tag{18}$$

where k_m is the intrinsic reaction rate constant per unit mass of the swollen catalyst particle. For catalyst particles of two different sizes d_1 and d_2 ($d_1 < d_2$),

$$\frac{\Phi_2}{\Phi_1} = \frac{d_2}{d_1} \tag{19}$$

$$\frac{\eta_1}{\eta_2} = \frac{(r_m)_2}{(r_m)_1}, \tag{20}$$

where $(r_m)_1$ and $(r_m)_2$ are apparent reaction rates obtained experimentally for the particle sizes d_1 and d_2, respectively. It is possible to obtain the values of Φ and η for each catalyst particle size by the method of particle size variation (trial and error) using the data in Table 3. The values of Φ and η obtained are listed in Table 3. It is evident that the value of η decreased with an increase in the catalyst particle size.

The temperature effect on the initial rates of oxidation of 3,5-DtBC with Cu(II)–PVP catalyst of size range 0–74 μm over a temperature range of 283–308 K at a con-

TABLE 3

Rate Constants for 3,5-DtBC Oxidation Catalyzed by the Cu(II)–PVP System

Dry particle size range (μm)	$\bar{d}_p$ (dry) (μm)	d_p (swelling) (μm)	Rate of oxidation (mol/s · cm³)	k_p (cm/s)	k_s (cm/s)	η	Φ
0–74	37	50	8.08×10^{-9}	8.22×10^{-6}	1.10×10^{-5}	0.98	0.18
74–149	112	152	7.96×10^{-9}	2.10×10^{-5}	4.12×10^{-5}	0.85	0.56
149–250	200	271	6.28×10^{-9}	2.19×10^{-5}	1.52×10^{-4}	0.62	1.00
250–850	550	740	5.96×10^{-9}	5.34×10^{-5}	4.00×10^{-4}	0.32	2.70

stant oxygen pressure of 1 atm are illustrated in the form of an Arrhenius plot (Fig. 10). The apparent activation energy for 3,5-DtBC oxidation catalyzed by the Cu(II)–PVP system was calculated to be 65.1 kJ/mol from the slope of the straight line.

Reuse of Cu(II)–PVP catalyst. The recovery of the homogeneous catalysts by separation from the reactants and products is usually difficult and results in a considerable loss of the catalyst (sometimes it may include the expensive metal). Furthermore, in many cases, the homogeneous catalytic materials are not reusable. These difficulties with homogeneous catalysts may be circumvented by using a homogeneous catalyst in a heterogeneous form which is produced by binding a homogeneous catalyst to an inorganic carrier material or organic polymer. Initially, the amount of oxygen absorbed with reaction time in 3,5-DtBC oxidation was measured by means of a fresh Cu(II)–PVP catalytic system (first run). After the reaction, the solution was washed with methanol. This used Cu(II)–PVP catalyst was tried as a catalyst for the oxidation of 3,5-DtBC (second run). It was found that both plots lay nearly on the same line. (The oxygen absorption rates by fresh and used catalyst were 8.1×10^{-9} and 8.0×10^{-9} mol/s · cm, respectively.) The electronic absorption spectrum of the filtrate of the reaction solution, in which the Cu(II)–PVP catalyst was separated by filtration, was measured to determine whether Cu(II) ions were eluted from the Cu(II)–PVP catalyst during oxidation of 3,5-DtBC. Cu(II) ions were not detected in the filtrate. From these results, the Cu(II)–PVP catalyst was considered reusable for 3,5-DtBC oxidation.

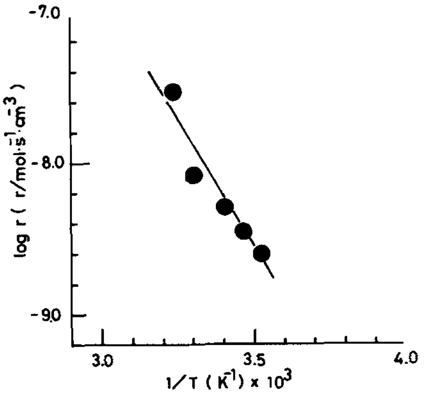


FIG. 10. Arrhenius plot of initial rate of 3,5-DtBQ production catalyzed by Cu(II)–PVP: catalyst, 1.0 g (37 μm); CH_3OH, 25 ml; temperature, 303 K; 600 rpm; O_2 atmosphere.

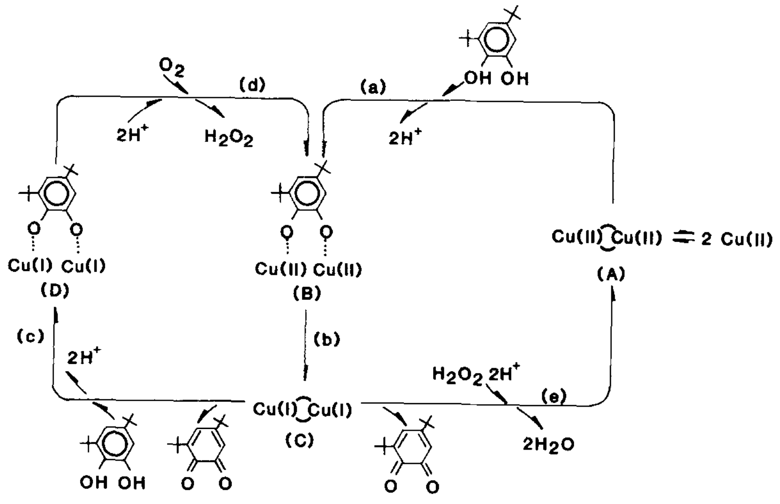
DISCUSSION

Homogeneous Cu(II) chelate catalyst. The Cu(II) chelates used in these experiments as catalysts were found to yield only the dehydrogenation product 3,5-DtBQ; no other oxygenation product such as a muconic acid derivative was detected. The catalytic activity for 3,5-DtBC oxidation decreased in the following order: $Cu(acac)_2 > Cu(salad)_2 > Cu(dmg)_2 > Cu(acacen)$. It has been reported that the coordination of Cu(II) ion through the nitrogen atoms in a chelate ligand is more stable than that through the oxygen atoms in a chelate ligand. Thus, the difference of the catalytic activity with the copper(II) chelate might be caused partly by the difference of the stability of the Cu(II) chelate complexes (*23*). The strength of the interaction of substrates, 3,5-DtBC with the Cu(II) chelate catalyst, may depend on the stability between the Cu(II) ion and the chelate ligands.

As illustrated in Fig. 4, a good correlation was found between log k and the pK_a of the pyridine derivatives added to the $Cu(acac)_2$ catalyst. It is clear that the rate constant, k, increased when the basicity of the pyridine derivative was increased. It is of interest to consider the relationship between the catalytic activity for 3,5-DtBC and the stability of the Cu(II) chelate–pyridine derivatives or the Cu(I)-O_2 adducts. James and his co-workers (*27*) have presented the thermodynamic data for ligands (L) binding to cobalt(II) protoporphyrin IX dimethyl ester (CoP), and compared the data for the formation of the five-coordinate complex

LCoP with the thermodynamic data for the reversible binding of oxygen (1 : 1) to LCoP. From their study, it was demonstrated (*27, 28*) that good correlations are found between log K_{O_2}, log K_1, and the pK_a of the protonated pyridine bases if the ligand is restricted to structurally related para-substituted pyridine ligands, where K_1 and K_{O_2} are the equilibrium constants of CoP + L $\rightleftharpoons$ LCoP and LCoP + O_2 $\rightleftharpoons$ LCoP(O_2), respectively. Thus, both log K_{O_2} and log K_1 have been found to increase with increasing pK_a values of the para-substituted pyridine ligands. The facts obtained with cobalt(II) systems can be applied to the discussion of the role of the pyridine derivatives added to the Cu(acac)$_2$ catalyst in 3,5-DtBC oxidation, although both CoP and Cu(acac)$_2$ systems are fairly different from each other both electronically and sterically. From the comparison of the effect of the added pyridine derivatives on the rate constant k (Fig. 4) with the results (*27*) obtained by James and his co-workers, it might be inferred that the stability of Cu(acac)$_2$–pyridine derivatives and the strength of the interaction between the Cu(I) dimer and O_2 molecules are the important factors affecting the catalytic activity for 3,5-DtBC oxidation. Recently, Drago and his co-workers (*29*) have reported both steric and electronic effects of ligand variation on cobalt–dioxygen catalysts. According to the results observed by ESR cobalt hyperfine coupling constants of the adducts and the electronic effects of substituents, the activity of the cobalt–dioxygen catalyst roughly parallels the trends in basicity of the bound O_2. The order of the activities of Cu(acac)$_2$–pyridine derivatives for 3,5-DtBC oxidation is consistent with the trends in basicity of the bound O_2 if the interaction between the copper(I) and oxygen molecule are assumed to be the rate-determining step of the 3,5-DtBC oxidation (step (d) in Scheme 1). In addition to the interaction of pyridine derivative with the copper complex, the pyridine derivative can also interact with the substrate, 3,5-DtBC, which may be partly dissociated. These partly dissociated species are considered to interact more easily with the Cu ions (*50*).

The rate of the Cu(acac)$_2$-catalyzed oxidation of 3,5-DtBC is independent of the 3,5-DtBC concentration, but shows second-order dependence on the copper concentration and first-order dependence on oxygen concentration. Also, under a nitrogen atmosphere, it was found that 3,5-DtBC can be oxidized by the homogeneous Cu(acac)$_2$ or Cu(acac)$_2$–pyridine systems



SCHEME 1

which act as oxidants for 3,5-DtBC oxidation. It was also observed from electronic absorption spectra of the degassed reaction mixture of 3,5-DtBC and Cu(acac)$_2$ catalyst in an *in situ* cell that the copper(II) ions in the absence of oxygen were changed to the copper(I) ions. From the results obtained above, a reaction involving the steps shown in Scheme 1 may be suggested as a plausible scheme for 3,5-DtBC oxidation catalyzed by the Cu(II)(acac)$_2$–pyridine system.

In Scheme 1, (A) represents the dimeric copper(II) species and (B) and (D) are the copper(II)$_2$–3,5-DtBC and copper(I)$_2$–3,5-DtBQ adducts, respectively. In the first step, the copper(II) species form the corresponding dimeric copper(II) species (A), which are considered as active species for 3,5-DtBC oxidation. At present, however, we have no information on the structure and characterization of the dimeric copper species. The second-order dependence on the copper(II) catalyst concentration can be explained if the formation of the dimeric copper(II) species is reversible. The active dimeric copper(II) species interact with a 3,5-DtBC molecule to form species (B). The Cu(II) dimer–catechol reaction has been suggested as a critical step in the copper-catalyzed oxidation of catechols to quinones (*33, 34, 38, 40*). It has also been reported that the cupric ion clearly functions as an electron acceptor in this oxidation reaction (*33, 34, 38, 40*). Step (b) is an intramolecular electron-transfer step of the adduct (B) to generate the oxidation product, 3,5-DtBQ, and the reduced Cu(I) dimer. Different processes of electron-transfer in the oxidation of catechol catalyzed by copper(II) complexes have been suggested by some workers. A simultaneous, two-electron transfer from the catecholate ion to two cupric ions has been suggested in the oxidation of catechol to benzoquinone (*30, 32, 33, 40*). Recently Thompson and Calabrese have reported (*48, 51*) that the oxidation of catechol proceeds in two one-electron transfer steps with a semiquinone intermediate, rather than in a single two-electron transfer step. Step (c) is the reaction between the reduced Cu(I) dimer and 3,5-DtBC to form a reduced Cu(I)$_2$–3,5-DtBC adduct (D). The rate-determining step is the reoxidation of the copper(I)$_2$ adduct (D) with an oxygen molecule to regenerate the copper(II)$_2$–3,5-DtBC adducts and hydrogen peroxide (step (d)). Oxygen molecule has been reported (*33, 38, 40*) to be used to reoxidize cuprous ion produced during the catalytic reaction but unnecessary for substrate oxidation. Reproduced adduct (B) again generates 1 mol of 3,5-DtBQ and the reduced Cu(I) dimer (C), which, in the presence of hydrogen peroxide, is oxidized to the Cu(II) dimer (A) through step (e). In this step, H_2O is also formed as shown in Scheme 1. The Cu(II) dimer produced in step (e) reacts with 3,5-DtBC to complete the subsequent catalytic cycle; (a) → (b) → (c) → (d) → (b) → (e) → (a). A part of Cu(II)$_2$–3,5-DtBC species (B) formed by step (d) may yield 3,5-DtBQ through step (b) ((d) → (b)), in place of step (e) ((d) → (e)). The first-order, the second-order, and the zero dependences on the partial pressure of oxygen, the copper(II) concentration, and the concentration of 3,5-DtBC, respectively (Eq. (2)), can be interpreted by Scheme 1 presented here. The catalytic cycle in Scheme 1 also satisfies the experimentally obtained stoichiometry of 3,5-DtBC oxidation catalyzed by Cu(acac)$_2$ or the Cu(acac)$_2$–pyridine system: 3,5-DtBC + $\frac{1}{2}O_2 \rightarrow$ 3,5-DtBQ + H_2O.

Heterogeneous Cu(II)–PVP catalyst. Only 3,5-DtBQ, the dehydrogenation product, was yielded by the heterogeneous Cu(II)–PVP catalyst. The influence of the amount of Cu(II) on the PVP support in the catalytic activity for 3,5-DtBC oxidation is worth remarking. As previously described, the oxidation activity, based on the Cu(II) ion on the Cu(II)–PVP catalyst, of the catalyst supported by the smaller amount of the Cu(II) ions was found to be larger than the oxidation activity of that supported by the larger amount of Cu(II) ions. This result may indicate that the active sites in the heterogeneous Cu(II)–PVP catalyst are the Cu(II)–pyridine moieties in which the mole ratio of Cu(II) ion to coordinated pyridine moieties is relatively low.

Careful analyses of the kinetic data might be required to elucidate the reaction scheme of the solid catalytic system suspended in liquid (slurries) because of mass transfer, particularly for the large catalyst particles. It is worthwhile to investigate systematically and quantitatively the influence of the mass transfer on the oxidation activity. The effect of the size of the catalyst particles was at first studied in order to evaluate the mass transfer effect on the 3,5-DtBC oxidation rate. As expected, the smallest particle size ($\bar{d}_p = 37\ \mu m$) had the highest effectiveness factor, 0.98, and the lowest value for the Thiele modulus, 0.18. The smaller particle size of the Cu(II)–PVP catalyst increased the rate of 3,5-DtBC oxidation and the effectiveness factor η (Table 3). Also, the fraction of the mass transfer resistance of the total resistance of the reaction and the mass transfer ($1/k_p/(1/k_p + 1/k_s)$) were found to decrease with a decrease of the Cu(II)–PVP catalyst particle size. Thus, from the relationship between the effectiveness factor and the obtained Thiele modulus, it is concluded that mass transfer is a major factor in determining the overall rate at which 3,5-DtBC is oxidized to 3,5-DtBQ by the large particle size of the heterogeneous Cu(II)–PVP catalyst. In the case of small particle size, the surface reaction is the major factor in controlling the overall rate.

Comparison between homogeneous and heterogeneous Cu(II) complex catalysts. The apparent activation energy of 3,5-DtBC oxidation catalyzed by the heterogeneous Cu(II)–PVP system was 65.1 kJ/mol, in comparison with the value of the homogeneous $Cu(acac)_2$–pyridine of 15.7 kJ/mol. As described under Results, the initial oxidation activity for the heterogeneous Cu(II)–PVP catalyst was found to be appreciably lower than that of the homogeneous Cu(II) complex catalyst. Despite the lower initial oxidation activity of the heterogeneous Cu(II)–PVP catalyst, this catalytic system seems to have an advantage of prolonging activation beyond that of the homogeneous Cu(II) complex catalyst, which has a tendency to deactivate with reaction time. Furthermore, since hardly any Cu(II) ions eluted from the Cu(II)–PVP catalyst and the used catalyst had nearly the same oxidation activity for 3,5-DtBC as it did in the fresh state, the heterogeneous Cu(II)–PVP catalyst was found to be useful for 3,5-DtBC oxidation under the present reaction conditions.

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