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Oxidation of hydrophobic hydroquinone by polyvinylpyridine-Cu(II) complex catalyst

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SUMMARY

A hydrophobic hydroquinone, 2,5-di-tert-butylhydroquinone (DTBHQ) was oxidized by polyvinylpyridine(PVPy)-Cu(II) complex catalyst in order to clarify the importance of the adsorption of substrate in the O_2 oxidation of hydroquinones. Contrary to our expectation, the activity of the polymer catalyst was lower than that of the low molecular weight catalyst. In Michaelis-Menten kinetic, the k_{cat} values of the PVPy-Cu(II) complex catalyst in the oxidation of DTBHQ were higher than that of the pyridine-Cu(II) complex catalyst as same as to the case of hydroquinone (HQ) oxidation, however the K_m values of the polymer catalysts were about 20 times larger than that of pyridine complex catalyst. Since DTBHQ was hard to be adsorbed into the active site due to its steric hindrance, the polymer catalyst had lower activities than the pyridine complex catalyst.

INTRODUCTION

The oxidation by the polymer ligand - metal complex catalyst is considered as a noteworthy reaction, in which a polymer catalyst had higher activity than a low molecular weight catalyst(1,2). It was reported that, in the oxidation of HQ or ascorbic acid by the Cu(II)-O_2 system, PVPy-Cu(II) complex catalyst had a remarkably higher activity than pyridine-Cu(II) complex catalyst(3). The reasons why the polymer catalyst had high activity were explained as follows: 1) Pyridine polymer adsorbed substrates(4,5): 2) The reoxidation step of Cu(I) which was produced in the process of substrate oxidation was accelerated in the polymer complex(2,6).

In our preceding study(7), it has become clear that substrates were adsorbed in the active site by a hydrophobic interaction between the substrate and the polymer main chain and/or by a hydrogen bonding between HQ and pyridine rings, and that the adsorption of substrates was influenced by the polarity of the solvent. This study aims to explain the mechanism of the oxidation of more hydrophobic substrate, DTBHQ, which is believed to exhibit a more hydrophobic interaction to the polymer main chain than HQ, and the results of detailed study of the adsorption effect are presented.

RESULTS AND DISCUSSIONS

Synthesis of the substrate DTBHQ and the oxidized compound DTBBQ

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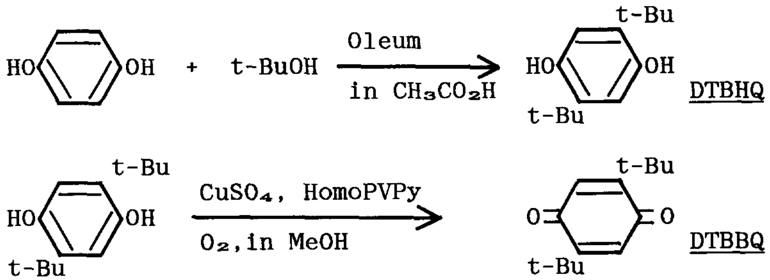
Hydrophobic substrate DTBHQ was synthesized according to the previous procedure(8).(Scheme 1) For the kinetic studies of this oxidation, 2,5-di-tert-butylbenzoquinone(DTBBQ) as an authentic compound of the reaction product was synthesized by the oxidation of DTBHQ using PVPy-Cu(II) complex as a catalyst. The oxidation was carried out in methanol(MeOH) under O_2 bubbling. After the reaction, MeOH was removed under the reduced pressure, and the residual polymer was washed with the excess amount of diethyl ether(Ether) and removed by filtration. The oxidized product was easily taken out from the filtrate by evapolation with appropriate yield.



Scheme 1

Oxidation of DTBHQ

For the purpose of explicating the effect of substrate adsorption, hydrophobic hydroquinone, DTBHQ, was oxidized in a same manner as HQ oxidation. The results are shown in Table 1 with the results of HQ oxidation(7).

DTBHQ was easily oxidized to corresponding benzoquinone, DTBHQ, even in the controlled reaction as compared with HQ. In the oxidation of DTBHQ, pyridine-Cu(II) complex had a higher observed rate constant k_{obsd}, than Cu(II) alone as well as in the case of HQ oxidation. Contrary to our expectation, a low catalytic activity was obtainedin the case of homoPVPy-Cu(II) complex.

In order to explain the reason why the polymer had lower activity than pyridine complex, we made two assumptions as folows; 1) The turnover of catalyst was inhibited by the oxidized product which remained around the active site because of hydrophobic interaction. 2) The bulky substrate, DTBHQ, could not be adsorbed into the PVPy-Cu(II) complex due to its steric hindrance. We carried out the Michaelis-Menten kinetic treatment for DTBHQ oxidation to clarify the above assumption. It was reported that the Cu(II) complex catalyzed oxidation of HQ or ascorbic acid proceeded via a typical Michaelis-Menten mechanism(4,9). Figure 1 is a plot of Lineweaver-Burk treatment in H_2O/MeOH (v/v=1/3) cosolvent. In the presence of

Table 1
Obserbed Rate Constants for the Oxidation of DTBHQ

Ligand	$10^5 \cdot k_{obsd}$(1/s) DTBHQ	 $HQ^{a)}$
None	62.4	1.6
Pyridine	119.5	3.4
HomoPVPy	32.4	44.3

Oxidized in H_2O/MeOH(v/v,1/3) at 25℃ [DTBHQ]=4.4×10^{-4}M
[DTBHQ]:[Py unit]:[Cu(Ⅱ)]= 10:10:1
a) Ref.(7)

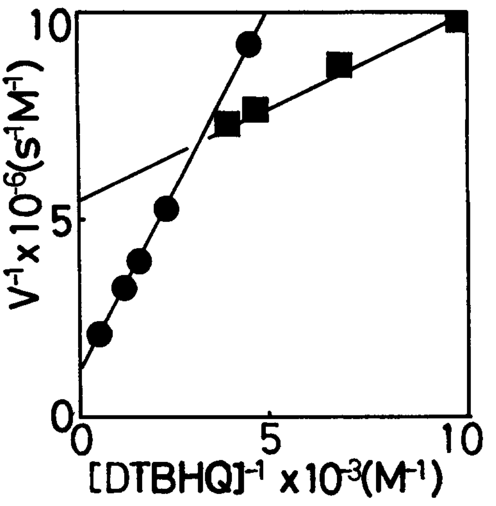


Fig.1 Lineweaver-Burk Plot of the Oxidation of DTBHQ
(●):HomoPVPy, (■):Pyridine

Table 2 Kinetic Parameters for the Oxidation of DTBHQ

Ligand	$10^4 \cdot$Km (M)	$10^2 \cdot k_{cat}$ (1/s)	k_{cat}/Km (1/s·M)
Pyridine	0.9	2.1	234.1
HomoPVPy	17.6	11.2	63.4

Oxidized in H_2O/MeOH(v/v,1/3) at 25℃
$[CuSO_4]=8.89x10^{-6}M$, [Py unit]$=8.86x10^{-5}M$

pyridine or homoPVPy, both plots gave a straight lines (correlation coefficient R> 0.99). These results indicated that the kinetic treatment based on the Michaelis-Menten mechanism was also appropriate for the oxidation of DTBHQ.

K_m and k_{cat} values calculated from the slopes and the intercepts of the straight lines in Figure 1 are summarized in Table 2. k_{cat} values of the polymer catalyst were larger than that of the low molecular weight analogue. In the oxidation of HQ the K_m value of the pyridine complex was about 10 times larger than that of polymer catalyst (10). The results indicated that the polymer complex catalyst had highly catalytic activity owing to the effect of adsorption of substrates. However, in the oxidation of DTBHQ, the K_m values of the polymer catalysts were about 20 times larger than that of pyridine complex catalyst. These results indicated that DTBHQ was hard to be adsorbed into the active site. In spite of larger k_{cat} value of the polymer catalyst, k_{obsd} was lower than that of a low molecular weight catalyst. These kinetical values suggest that bulky DTBHQ can not closely approach the active site owing to the steric hindrance around Cu(II) complex. Furthermore homoPVPy-Cu(II) complex catalyst had a lower activity than Cu(II) alone, because the free Cu(II) ions which could oxidize bulky DTBHQ might have decreased by complexing with polyVPy ligand.

In conclusion, more hydrophobic DTBHQ was used as a substrate in the oxidation by polyVPy-Cu(II) complex catalyst, since we anticipated the effect of substrate adsorption. However, the polymer catalyst had a lower activity. In the oxidation of DTBHQ, despite the higher k_{cat}, the polymer catalyst had only a lower catalytic activity because of its lower adsorption efficiency for substrates by the steric hindrance. It became clear that the adsorption effect was one of the important factors which affected a catalytic activity of PVPy-Cu(II) complex catalyst.

EXPERIMENTAL

Materials

4-VPy was purified by distillation just before polymerization. HQ and other reagents were obtained commercially and used without further pulification. Polymeric ligand, homoPVPy was synthesized as our previous reported method(7).

Synthesis of 2,5-di-tert-butylbenzoquinone(DTBBQ)

DTBHQ was synthesized by Oesper's method(8). The product was recrystallized twice from benzene; yield of DTBHQ, 16.2g(80%), mp.:214.0-215.0°C(lit.(8) 210-212°C)

DTBBQ was synthesized by the oxidation of DTBHQ using polyVPy-Cu(II) complex catalyst in MeOH. Namely, in a 200ml of three-necked flask equipped with a magnetic stirrer, a condenser, and a gas inlet tube, 0.1mmol of $CuSO_4$, 0.056g(0.5mmol vinylpyridine unit) of homoPVPy, and 50 ml of MeOH were placed. The 4.5 mmol of DTBHQ was added and the solution was stirred for 2 hr at 45°C under O_2 bubbling. Then, the solvent was removed under vacuum and the precipitated polymer complex was washed with excess amount of Ether and filtered off. The filtrate was dried over sodium sulfate and Ether was removed under reduced pressure. The residue was recrystallized twice from petroleum ether; yield of DTBBQ: 66%, mp.148.0-149.5°C(lit(11):150-151°C); IR(KBr):1650 cm^{-1}($>C=O$); ^1HNMR ($CDCl_3$): δ =6.45(s,2H, ), δ =1.23(s,18H,$-C(CH_3)_3$); λ_{max}=256 nm, ε_{max}=17850 in H_2O/MeOH(1/3)(lit(11) λ_{max} = 254nm, ε_{max} = 18383 in EtOH)

Kinetic procedure of the oxidation

PolyVPy-Cu(II) complex was prepared by stirring polyVPy and $CuSO_4$ in H_2O/MeOH(v/v=1/3) cosolvent for 30 min just before oxidation at 25°C. Then pure oxygen was bubbled into the solution. The oxidation started immediately after the substrate (DTBHQ) was added. Pseudo-first-order rate constants(k_{obsd}) of the oxidation were obtained from the absorbance at λ_{max} of DTBBQ on a Hitachi U-2000.

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