Catalytic Activity of Anion-Exchange Resins Modified with Metal-Porphine in Oxidative Reactions of Phenols

Akimasa IWADO,a Masaki MIJUNE,b Jiro KATO,b Junko ODA,a Masahiko CHIKUMA,c Noriko MOHOASHI,d and Yutaka SAITOa,b

The Graduate School of Natural Science and Technology, Okayama University,* Tsushima-Naka, Okayama 700–8530, Faculty of Pharmaceutical Sciences, Okayama University,* Tsushima-Naka, Okayama 700–8530, Osaka University of Pharmaceutical Sciences,c Nasahara, Takatsuki 569–1094, and Kobe Pharmaceutical University,d Motomakita-machi, Higashinada-ku, Kobe 658–8558, Japan.

Received June 22, 2000; accepted August 6, 2000

Anion-exchange resins modified with metal–porphine (M–P) have been investigated to develop a solid catalyst in the oxidative reaction of phenols by O₂ in air. Co–P, which is easily prepared and separable from the reaction mixture, has been proved to accelerate the oxidative reaction of phenols such as 3,5-di-tert-butyl-4-hydroxyanisole. The resulting main oxidative products were identified to be quinones by using the GC–MS method.

Key words oxidation catalyst; immobilized metal–porphine; oxidation of phenols

Metal complexes of porphines1) and salens2) have been studied as oxidation catalysts in the oxidative reaction of phenols. Recent studies on metal-phthalocyanine functionalized silicas3) and metal-salens encapsulated in zeolite5) have provided noteworthy approaches to the development of a solid catalyst. Our previous studies on the catalytic activities of ion-exchange resins modified with metal–porphine (M–P) have revealed that Co– and Mn–P exhibit potent activities in oxidative reactions of uric acid and ascorbic acid by O₂ in air.6)–10) We have continuously studied the catalytic activity of M–P, in oxidative reactions of phenols. In the present paper, we report that Co–P, accelerates the oxidative reaction of phenols to a quinones as a solid catalyst.

Experimental

The H₂–porphines shown in Fig. 1 were converted into metal–complexes (M–P, M=Co, Mn, Fe, and Cu) by the methods described in the literature.11,12) M–P, in which 50 μmol of M–P was modified on 1.0 g of dry Amberlite IRA 900 (24–42 mesh) or dry Dowex MSC-1 (20–50 mesh), was prepared according to the simple method reported previously.13)–14)

Commercially available 3,5-di-tert-butyl-4-hydroxyanisole (DBHA), 2,6-di-tert-butyl-4-methoxyphenol (DBMP), and 2,6-di-tert-butylphenol (DBP) were purified by recrystallization. Authentic quinones used as standards were obtained from commercial sources and prepared by the methods published in the literature (see Notes).

GC–MS was measured by the electron-impact (EI) ionization method on a VG-70 SE mass spectrometer equipped with a Hewlett Packard 5896 GC instrument.

For evaluation of the oxidative catalytic activity, M–P (100 mg) was added to a methanol solution of phenols (5 mm, 10.0 ml), and the mixture was incubated at 35 °C for 1 h. The unchanged phenols and generated products in the supernatant, which was easily separable from M–P, were determined by the GC method using DBMP as an internal standard. For check of repeated uses, incubation was carried out for 2 h per use.

Results and Discussion

Figure 2 represents the time course of DBHA level in the reaction mixture, which shows that most of the DBHA was consumed after 2-h incubation with Co–TSPP. Figure 3 represents a GC chart of the reaction mixture after 3-h incubation with Co–TSPP. As seen from Fig. 3, an extremely small peak of DBHA at 9.9 min and a very strong peak attributed to a main product at 7.2 min were observed. When the MS of the peak at 7.2 min was measured, a medium peak at 220 amu, which may be attributed to the ion of [2,6-tert-butyl-1,4-benzoquinone (rBBQ)]⁺, was observed. In addition, the MS fragment pattern and the retention time of the main product agreed with those obtained from a commercially available rBBQ. We therefore identified the product as rBBQ, which has been reported to be one oxidative product of DBP.11) Furthermore, since no decrease of DBHA was ob-

Fig. 1. Structures of H₂–Porphines

Fig. 2. Time Course of DBHA Level during Treatment with Co–TSPPr

GC Conditions: an OV-1 column (0.5 mm×50 m), 150→250°C (8°C/min).

Fig. 3. GC of the Reaction Mixture Incubated for 3.0 h at 35°C

GC Conditions: an OV-1 column (0.5 mm×50 m), 150→250°C (8°C/min).

* To whom correspondence should be addressed. e-mail: saito@pharm.okayama-u.ac.jp © 2000 Pharmaceutical Society of Japan
served under an N₂-atmosphere, we confirmed that DBHA was mainly oxidized to rBBQ by O₂ in air.

Table 1 shows the unchanged DBHA (%) in the reaction mixture after treatment for 1 h with the individual modified resins. Co³⁺–TSP, resulted in the largest change of DBHA among the modified resins tested. When H₂–TSP, was used, 90% of DBHA remained unchanged even after 4-h treatment under the same conditions, which strongly suggests that the reaction is catalyzed by cobalt-ion in Co–TSP. When Fe³⁺– and Cu²⁺–TSP, were used, almost 100% of DBHA remained unchanged, as seen from Table 1, suggesting that the central metal ions in the porphine ring are essential for the oxidation reaction of DBHA. It is of interest that M–TMPyP, exhibited no notable activity. These results indicated that the oxidative activity of M–P, depends not only on the central metal ion but also on side chains of the porphine ring. In the present study, since Co–TSP, showed the highest activity among the M–P, tested, we decided to examine the activities of Co–TSP, in detail.

To confirm that Co–TSP, acts as a catalyst in the oxidative reaction of DBHA, its activity in the repeated uses was determined. After 10 time uses, Co–TSP, still had sufficient catalytic activity. This means that Co–TSP could catalyze at least 100-fold moles of DBHA, since the molar ratio of Co–TSP on the resin to DBHA in the initial reaction mixture was 1:10. Thus we concluded that Co–TSP, serves as a catalyst in the oxidative reaction of phenols. Furthermore, we compared the rate constants of phenol disappearance (k) catalyzed by Co–TSP, in methanol to those in CH₃CN used in previous studies. As a result, the k-value for DBHA in methanol was more than three times higher than that in CH₃CN. This result suggests that methanol is superior to CH₃CN as a solvent for Co–TSP.

In addition to DBHA, we have investigated the catalytic activity of Co–TSP, on DBMP and DBP by using methods similar to those described above. As a result, 85% of DBP was oxidized after 24-h incubation with Co–TSP. The oxidative products included rBBQ (equivalent to 68% of DBP) and 3,3',5,5'-tetra-tert-butylidiphenoxinoquinone (15% of DBP). This result is of interest from the view point of immobilization of the catalytic activity of Co–porphine, because the oxidative reaction of DBP was not catalyzed by Co–TPP (see Fig. 1) solution in CH₃CN after 24-h incubation. In the case of DBMP, although 100% of DBMP was converted into two main oxidative products, we could identify only 2,6-di-tert-butyl-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one (equivalent to 57% of DBMP).

In conclusion, Co–TSP, exhibited the catalytic activity in the oxidative reactions of phenols such as DBHA, and is expected to be not only a practically applicable solid catalyst but also a model of diphenol oxidases active on catecholamines such as epinephrine and dopamine.

Acknowledgments The authors thank to Professor J. Odo for his discussion at the initial stage. This work was supported by a Grant-in-Aid for Science Research from the Japan Society for the Promotion of Science.

References and Notes

13) Authentic compound, which was prepared by the method reported in J. Am. Chem. Soc., 81, 6335 (1959) by H. D. Kaese et al., was identified by using IR, ¹H-NMR, MS, and element analysis.
14) Authentic compound, which was prepared by the method reported in Bull. Chem. Soc. Jpn., 48, 1683 (1975) by A. Nishinaga et al., was identified by the methods of ¹H-NMR, IR, and element analysis.