The Autoxidation of Phenols Catalyzed by Phthalocyanine-Fe(II) and Salcomine-pyridine

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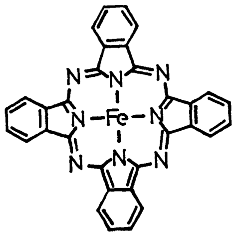
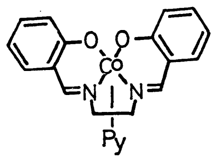
The autoxidation of 2,4,6-tri-*t*-butylphenol (**1**), 2,6-di-*t*-butylphenol (**2**), and 2,4-di-*t*-butylphenol (**3**) is catalyzed by phthalocyanine-Fe(II) (PC-Fe(II)) and salcomine-pyridine (SAL-Py). PC-Fe(II) gives, preferentially, the coupling product of such phenoxy radicals as **4**, **7**, and **8**. SAL-Py, on the other hand, gives *o*- and *p*-benzoquinones, such as **5** and **6**, resulting from the coupling of the phenoxy radical and the hydroperoxy radical. Metal phthalocyanines including Mn(II), Co(II), Ni(II), or Cu(II) as the central metal ion are inactive as catalysts for the oxidation. PC-Fe(II) does not catalyze the autoxidation of phenol itself and mono-alkylated phenols.

The autoxidation of phenols catalyzed by salcomine and its derivatives has drawn much attention in connection with the relation between the mode of oxidation and the states of the oxygen-adducts of salcomine.[1,2] On the other hand, the autoxidation of phenols catalyzed by ion complexes, which are assumed to be carriers of molecular oxygen, has not been reported except for the preliminary result on the autoxidation of poly-phenol catalyzed by phthalocyanine-Fe(II) (PC-Fe(II) hereinafter).[3] Our attention was directed to the catalytic activity of PC-Fe(II) in the autoxidation of organic compounds in connection with the structual similarity of PC-Fe(II) to a biologically-important hemin. In this paper we will report on the autoxidation of phenols catalyzed by PC-Fe(II). The autoxidation of phenols catalyzed by salcomine-pyridine (SAL-Py hereinafter) was also carried out in order to compare the modes of catalysis of the two catalysts.



PC-Fe(II)



SAL-Py

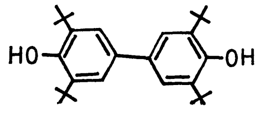
Results and Discussion

Several metal phthalocyanines including Mn(II), Co(II), Ni(II), or Cu(II) as the central metal ion were tested as catalysts for the oxidation 2,4,6-tri-*t*-butylphenol (**1**) and 2,6-di-*t*-butylphenol (**2**), but they were nearly all inactive; only PC-Fe(II) showed a strong catalytic activity. In contrast, Vogt *et al.* reported that the oxidation of 2,6-dimethylphenol was catalyzed by salcomines and not by the complexes in which the central metal ion of salcomine was replaced by Mn(II), Fe(II), Ni(II), or Cu(II).[1]

The distributions of the products from the oxidation of 2,4,6-tri-*t*-butylphenol (**1**), 2,6-di-*t*-butylphenol (**2**), and 2,4-di-*t*-butylphenol (**3**) are shown in Tables 1, 2, and 3 respectively.

The oxidation products from the three phenols **1**, **2**, and **3**, originate almost exclusively from the coupling of two phenoxy radicals when the oxidations are catalyzed by PC-Fe(II). The peroxide, **4**, must be formed by the coupling of two phenoxy radicals from **1** at a para-position through the bridge of molecular oxygen, as a result of the steric hindrance of a direct coupling. The biphenoquinone, **7**, must be formed by the further oxidation of biphenol **9**. On the oxidation of **3**, the biphenol **8** is not further oxidized[4] and an appreciable amount of the starting phenol, **3**, is recovered; the yield of **8** is improved to 88% by changing the solvent from methanol to tetrahydrofuran.

On the oxidations of **1**, **2**, and **3** catalyzed by SAL-Py, the coupling of a phenoxy radical and a hydroperoxy radical becomes more important. Thus two quinones, **5** and **6**, from the phenol **1** must be formed through the intermediates, **10** and **11** respectively, by the elimination of *t*-butyl alcohol. The first oxidation products, **12** and **13**, from the phenols **2** and **3** respectively, must be further transformed to afford the quinones **5** and **6**.



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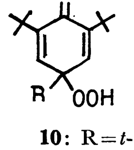
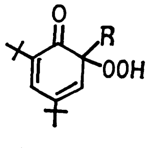


10: $R=t\text{-}C_4H_9$
12: $R=H$



11: $R=t\text{-}C_4H_9$
13: $R=H$

The mode of the autoxidation of *t*-butyl-substituted phenols catalyzed by PC-Fe(II) is similar to that of oxidations by a one-electron-transfer oxidizing agent, such as $K_3Fe(CN)_6$, PbO_2, or Ag_2O.[5,6,7] The autoxi-

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[1] a) L. H. Vogt, Jr., J. G. Wirth, and H. L. Eisenbeiner, *J. Org. Chem.*, **34**, 273 (1969). b) D. J. Tamaja, L. H. Vogt, Jr., and J. G. Wirth, *ibid.*, **35**, 2029 (1970).

[2] T. Matsuura, K. Watanabe, and A. Nishinaga, *Chem. Commun.*, **1970**, 163.

[3] A. H. Cook, *J. Chem. Soc.*, **1938**, 1768.

[4] A different product becomes the major one upon the catalysis of PC–Fe(II) which has been purified freshly by precipitation from a sulfuric-acid solution of PC–Fe(II) by adding water. The structure of this product is now under investigation.

[5] C. D. Cook and R. C. Woodworth, *J. Amer. Chem. Soc.*, **75**, 6242 (1953).

[6] H. Blanchard, *J. Org. Chem.*, **25**, 264 (1960).

[7] C. D. Cook, *ibid.*, **18**, 261 (1953).

Table 1. AUTOXIDATION OF 2,4,6-TRI-*t*-BUTYLPHENOL (**1**)

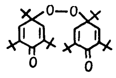
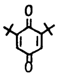
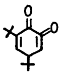
Catalyst	Product		
	 **4**	 **5**	 **6**
PC–Fe(II)	87%	4%	2%
SAL–Py	40%	28%	4%

Table 2. AUTOXIDATION OF 2,6-DI-*t*-BUTYLPHENOL (**2**)

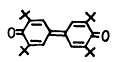
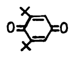
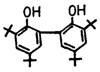
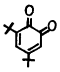
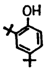
Catalyst	Product	
	 **7**	 **5**
PC–Fe(II)	*ca.* 100%	
SAL–Py	11%	75%

Table 3. AUTOXIDATION OF 2,4-DI-*t*-BUTYLPHENOL (**3**)

Catalyst	Product		
	 **8**	 **6**	 recovered
PC–Fe(II)[D]	57%	trace	36%
SAL–Py	3%	29%	58%

dation catalyzed by SAL-Py, on the other hand, gives quinones preferentially; this characteristic is rather similar to that of cobalt- or copper-complexes, such as salcomine or CuCl-amine which have a high potential to combine with molecular oxygen.[1,8,9]

PC-Fe(II) does not catalyze the autoxidation of phenol itself and mono-alkylated phenols including *o*- and *p*-*t*-butylphenol, and *o*-, *m*-, and *p*-cresol. PC-Fe(II) catalyzes only the oxidation of phenols giving stable phenoxy radicals, including di- and tri-*t*-butylphenols, and gives the products derived from the coupling of two phenoxy radicals, either directly or through an oxygen bridge.

Experimental

Materials. Commercially available 2,4,6-tri-*t*-butylphenol (**1**), 2,6-di-*t*-butylphenol (**2**), and 2,4-di-*t*-butylphenol (**3**) were used after purification by recrystallization from ethanol; **1**, mp 131°C, or distillation under reduced pressure; **2**, 132—133°C/18 mmHg, **3**, 141—142°C/18 mmHg.

Catalysts. Metal phthalocyanines were prepared by the method of Dent-Linstead[10] from the chlorides of the corresponding metal and phthalonitrile, or by Gattermann's procedure[11] from the corresponding chlorides, phthalic anhydride, and urea. The crude phthalocyanines were successively washed with boiling methanol, hot diluted sulfuric acid, methanol, and ether. The phthalocyanines thus obtained were dried and kept in a desiccator until their use.

Salcomine-pyridine was prepared by the procedure of Bails-Calvin[12] from cobalt acetate, ethylenediamine, salicylaldehyde, and pyridine; the complex was kept in a vacuum desiccator until its use.

A General Procedure of Autoxidation. A methanol solution (100 m*l*) of one of the phenols (0.015 mol) was exposed to oxygen for 18 hr at room temperature in the presence of metal phthalocyanine (0.015 mol) or salcomine-pyridine (0.015 mol). The reaction mixture was magnetically stirred during the reaction period. After the evaporation of the solvent, the product was taken into ether and was purified by preparative layer chromatography on silica gel eluted with benzene.

*Oxidation of 2,4,6-Tri-*t*-butylphenol (1).* The oxidation products from 0.393 g of **1** were seperated by preparative layer chromatography to give three bands on the chromatogram. The extraction of the top, middle, and bottom bands gave peroxide **4** (0.341 g, 87%), *p*-quinone **5** (0.016 g, 4%) and *o*-quinone **6** (trace) respectively when catalyzed by PC-Fe(II). The autoxidation of the phenol **1** by SAL-Py gave the same products as those from the PC-Fe(II) catalysis, but the product distribution was different, as is shown in Table 1. The structures of the products were deduced to be **4**,[13] **5**,[14] and **6**[15] from a comparison of their melting points and infrared spectra.

*Oxidation of 2,6-Di-*t*-butylphenol (2).* The oxidation product of 0.309 g of the phenol **2** catalyzed by PC-Fe(II) showed only one spot on an analytical thin-layer chromatogram without any purification; it was identified as biphenoquinone **7**[16] (0.306 g, *ca.* 100%) by a comparison of the melting points and infrared spectra. The oxidation product of 0.309 g of **2** catalyzed by SAL-Py showed two bands on a preparative layer chromatogram; the lower band gave *o*-quinone **5** (0.232 g, 75%) as the major product, while biphenoquinone **7** (0.033 g, 11%) was given from the upper band.

*Oxidation of 2,4-Di-*t*-butylphenol (3).* The oxidation product of 0.309 g of **3** catalyzed by PC-Fe(II) gave two spots on an analytical thin-layer chromatogram; the lower spot corresponded to the starting phenol **3** (0.111 g, 36%). The oxidation product, the upper spot, was seperated by preparative layer chromatography to give biphenol **8** (0.176 g, 57%), which was found to be identical with the authentic sample[17] by a comparison of the melting points and infrared spectra. Preparative layer chromatography of the product from the reaction catalyzed by SAL-Py showed another band at the bottom of the chromatogram. The extraction of that band afforded *o*-quinone **6** (0.089 g, 29%) as the major product.

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8) A. Nishinaga, K. Watanabe, and T. Matsuura, 4th Symposium on Oxidation, Chemical Society of Japan, October 1970, Tokyo, Abstract p. 48.

9) C. M. Orland, Jr., *J. Org. Chem.*, **33**, 2516 (1968).

10) C. E. Dent and R. P. Linstead, *J. Chem. Soc.*, **1934**, 1027.

11) L. Gattermann, "Die Praxis des Organischen Chemikers" 40 Auflage, Walter de Gruyter & Co., Berlin (1961), p. 288.

12) R. H. Bails and M. Calvin, *J. Amer. Chem. Soc.*, **69**, 1886 (1947).

13) E. Müller and K. Ley, *Chem. Ber.*, **87**, 922 (1954).

14) E. Müller and K. Ley, *ibid.*, **88**, 601 (1955).

15) K. Ley and E. Müller, *ibid.*, **89**, 1402 (1956).

16) M. S. Kharasch and B. S. Jhose, *J. Org. Chem.*, **22**, 1439 (1957).

17) J. H. Fookes, E. L. Pelton, and M. W. Long, Jr., U. S. Patent 2885444 (1959), *Chem. Abstr.*, **54**, 5579i (1970).