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Cobalt(II)-Catalyzed Oxidation of 2,6-Xylenol in Toluene

PAVEL HUDEC

Research Institute of Macromolecular Chemistry, 656 49 Brno, Czechoslovakia

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The oxidation of 2,6-xylenol with molecular oxygen has been studied using toluene as a solvent and bis(*n*-butyl-*N*-salicylideneiminato)cobalt(II) as a catalyst. The products of the oxidation were 3,5,3′,5′-tetramethyldiphenoquinone-4,4′ and low molecular weight poly(2,6-dimethylphenylene-1,4-oxide). During this reaction the irreversible oxidation of cobalt (II) chelate has been observed. A simple reaction scheme has been suggested to describe the complex kinetic behavior.

INTRODUCTION

Owing to its great industrial importance, the metal-catalyzed oxidation of 2,6-disubstituted phenols with molecular oxygen has been the subject of many papers. A large number of different oxidizing agents has been already used. Effective catalysts of this oxidation include cobalt(II) chelates, especially the *N*,*N*′-ethylenebis(salicylideneiminato)cobalt(II), and their derivatives (salcomines) (*1–5*). Lately the use of cobalt(II)-phthalocyanine (*6*, *7*), cobalt(II)-tetraphenylporphyrin (*6*), and cobalt(II)-dimethylglyoxime (*6*) has been reported in the literature. In these papers consideration has been predominantly given to the reaction conditions and products, whereas kinetic data are rather scarce. Recently in our institute it was found that bis(*n*-butyl-*N*-salicylideneiminato)-cobalt(II), whose extraordinary behavior in redox reactions has already been described (*8*), showed under certain conditions the ability also to catalyze xylenol oxidation. The subject of this paper is the kinetics and products of this reaction.

EXPERIMENTAL METHODS

Chelates bis(*n*-butyl-*N*-salicylideneiminato)cobalt(II) (CoB_2) and Tris(*n*-butyl-*N*-salicylideneiminato)cobalt(III) (CoB_3) were prepared according to Charles (*9*). The analyses of Co and N agreed with theoretical values. 2,6-Xylenol (Chemical Works Záluži, Czechoslovakia) was purified by zone melting and contained 0.01% of impurities. Toluene (Lachema, Czechoslovakia) was purified by distillation.

The oxidation of 2,6-xylenol was carried out under an atmosphere of pure oxygen in a stirred glass reactor. The amount of the absorbed oxygen was measured volumetrically, by means of a 50-ml graduated gas burette attached to this reactor. The measurements were carried out within the region where no influence of stirring on the rate of reaction was observed. Spectrometric measurements were performed on an ir spectrometer UR 10 (Zeiss, Jena), on a uv-VIS spectrometer Spectromom 202 (Hungary), and on a Varian E3 X-band EPR spectrometer with 100-kHz modulation. The tlc analyses were performed on

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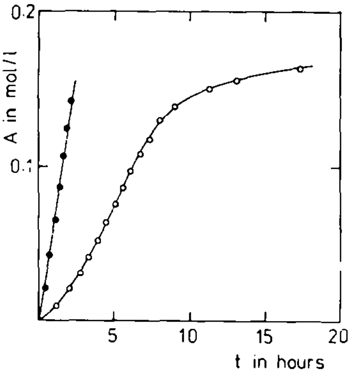
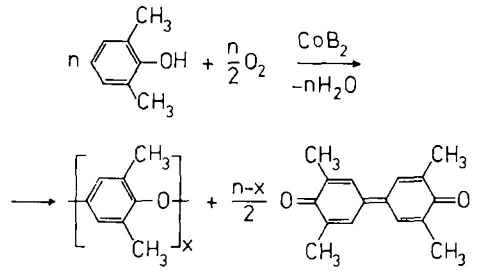


FIG. 1. Catalyzed oxidation of 2,6-xylenol. The experimentally found relation between the volume of absorbed oxygen A (moles/liter) and time. ○ with CoB_2 only, ● with CoB_2 in the presence of cyclohexylamine ($8\cdot10^{-2}$ mol/liter). $[\text{2,6-Xylenol}]_0 = 0.33$ mol/liter, $[CoB_2]_0 = 1.95\cdot10^{-2}$ mol/liter, temperature = 29.8°C.

activated layers of silica gel G. The mobile phase was a mixture of benzene and methanol, 95:5 (v/v). Co(II) was determined spectrophotometrically after extraction into the water layer as a thiocyanate complex.

RESULTS

Pure solutions of 2,6-xylenol in toluene show no perceptible oxygen absorption at temperatures of 20–40°C. Addition of 92 mg (0.22 mmol) of CoB_2 to 10 ml of toluene containing 1.19 g (9.76 mmol) of 2,6-xylenol caused the solution to absorb 108 ml (4.82 mmol) of oxygen during 24 hr, thereby giving the stoichiometric ratio 2,6-xylenol:oxygen of 2.03:1. No free 2,6-xylenol was found in the solution. Filtration of the reaction slurry gave 0.52 g of red precipitate. The ir and uv-VIS spectra of this compound were identical with the spectra of 3,5,3′,5′-tetramethyldiphenoquinone-4,4′. The identification was confirmed by tlc. The filtrate was diluted with the same volume of methanol. A white precipitate could be isolated (0.45 g). The ir spectrum of this precipitate was identical with the spectrum of poly(2,6-dimethylphenylene-1,4-oxide). The molecular weight determined viscometrically (*10*) was approximately $2\cdot10^4$. The remaining products obtained on evaporation of the reaction mixture were a Co(III) compound identified by means of ir, uv-VIS spectra and tlc as CoB_3, and a compound (0.19 g), the ir spectrum of which corresponded with the spectrum of low molecular weight polymer. Therefore, the CoB_2-catalyzed oxidation of 2,6-xylenol follows the stoichiometric equation:



(1)

The rate of oxygen absorption by 2,6-xylenol solutions in toluene was measured under the atmosphere of pure oxygen with various CoB_2 and 2,6-xylenol initial concentrations at various temperatures. The plot of absorbed oxygen vs time was an S-shaped curve with variable slope (see Fig. 1). The reaction rate determined from the tangent in the middle, approximately linear part of the curve was proportional to the square of the CoB_2 initial concentration. The reaction order relative to 2,6-xylenol initial concentration was not explicit. The relation between the rate of reaction and temperature passed through a maximum. In the course of the oxidation the initial red color of the solution gradually changed to green, indicating evidently the oxidation of Co(II) to Co(III). The decrease of Co(II) concentration was confirmed by direct analysis. The results are summarized in Table 1.

In order to throw more light on the rather complicated kinetic behavior, the reaction between molecular oxygen and CoB_2 chelate was studied by various methods in the absence of 2,6-xylenol. When oxygen was

TABLE 1

Rate of 2,6-Xylenol Oxidation at Various Temperatures and Various 2,6-Xylenol and CoB_2 Initial Concentrations

Temperature (°C)	29.8							
$[2,6\text{-Xylenol}]_0$ (mol/liter)	0.33							
$[CoB_2]_0 \cdot 10^2$ (mol/liter)	0.51	0.76	0.97	1.28	1.58	1.95		
Rate $\times 10^4$ (mol/liter·min)	0.18	0.50	0.71	1.45	2.0	3.06	3.10	3.14
$[2,6\text{-Xylenol}]_0$ (mol/liter)	0.047	0.11	0.15	0.20	0.25	0.30		0.33
$[CoB_2]_0 \cdot 10^2$ (mol/liter)	1.95							
Rate $\times 10^4$ (mol/liter·min)	1.9	2.1	2.2	2.4	2.5	2.7		3.0
Temperature (°C)		20	30	40	50			
$[2,6\text{-Xylenol}]_0$ (mol/liter)		0.33						
$[CoB_2]_0 \cdot 10^2$ (mol/liter)		1.87	2.01	1.90	1.90			
Rate $\times 10^4$ (mol/liter·min)		1.6	3.2	3.3	2.3			
$[CoB_2] \cdot 10^2$ (mol/liter) unreacted after 4 hr		1.60	1.78	1.86	1.90			

added to the toluene solution of CoB_2 in the cuvette of an EPR spectrometer, the EPR signal (octet) representing the interaction of an unpaired electron with the magnetic moment of the Co nucleus ($I = \frac{7}{2}$) was registered. Analogous spectra have already been reported in the literature and they have been assigned to adducts between molecular oxygen and cobalt(II) complexes with the stoichiometry 1:1 (*11*, *12*). Nevertheless, when pure and dry CoB_2 solutions in toluene were allowed in contact with molecular oxygen, no volumetrically measurable absorption was determined. Both the oxygen absorption and the oxidation of Co(II) to Co(III) were observed in the presence of moisture. The reaction was irreversible. The final molar ratio $CoB_2:O_2$ absorbed was found to be 1:0.24. The final products of this reaction were a chelate CoB_3 identified both by means of ir and uv-VIS spectra and by tlc and oxides of cobalt(III). The stoichiometry of this reaction may therefore be written as follows:

$$12CoB_2 + 3O_2 + 2H_2O \rightarrow 8CoB_3 + 4CoO(OH). \quad (2)$$

As water was one of the final products in 2,6-xylenol oxidation, it seemed very reasonable that the Co(II) decrease observed during this oxidation was the result of Reaction (2). It was verified that at the temperatures used the CoB_3 chelate had no effect on the 2,6-xylenol oxidation, and its rate was always proportional to the concentration of remaining CoB_2. Thus Reaction (2) simultaneously reduced the catalytic activity of the cobalt chelate.

The absence of an induction period and an increase of reaction rate was observed after a small addition of cyclohexylamine to the reaction mixture (Fig. 1). By means of ir and uv-VIS spectroscopy, the reaction product was found to be 2,6-dimethyl-1,4-benzoquinone.

DISCUSSION

The results show that the CoB_2-catalyzed oxidation of 2,6-xylenol is a complex process and that a rather complicated reaction mechanism should be expected. From the EPR measurements it has been concluded that in the initial reaction stages an adduct is formed between the CoB_2 chelate and oxygen. The volumetric measurements show that the concentration of this adduct should be very low. It is assumed from the external order of the oxidation with regard to the Co(II) initial concentration that the next step should be the reaction of this adduct with another

CoB_2 molecule, probably to give the $CoB_2 \cdot O_2 \cdot CoB_2$ complex. The primary radical products should be formed by the reaction of this complex with 2,6-xylenol.

$$CoB_2 + O_2 \rightleftarrows CoB_2O_2 \tag{3}$$

$$CoB_2O_2 + CoB_2 \rightarrow CoB_2O_2CoB_2 \tag{4}$$

$$CoB_2O_2CoB_2 + \text{2,6-xylenol} \rightarrow \text{radical products.} \tag{5}$$

On the basis of papers by Tkáč *et al.* (*13*) it is presumed that these radicals are fixed on the cobalt atoms, and that the reaction proceeds by a sequence of redox and exchange steps within the ligand sphere of the catalytic complex.

The interpretation of the reaction kinetics is complicated by the side reaction giving inactive Co(III) products and thereby decreasing the active cobalt concentration. Nevertheless, the complexity of kinetic relations cannot be ascribed to this irreversible reaction only. The observed Co(II) decrease cannot explain the curved relation between the rate of 2,6-xylenol oxidation and temperature (see Table 1). Evidently both the reaction rate increase in the initial stages of reaction and its unusual temperature dependence should be ascribed to the sequence of consecutive reactions within the catalytic complex.

The sensitivity of metal-catalyzed oxidations of phenols to the presence of amines is well known from the literature (*2, 14*). Amines enter the ligand sphere of the metal atom and substantially influence the chemical character of the catalytic complex. As a result there are changes both in kinetics and reaction products. This was found also with chelate CoB_2, if cyclohexylamine was added. A different reaction mechanism should be used to explain the benzoquinone formation. It is supposed the amine displaces the radicals fixed on the cobalt atom, and the oxidation of 2,6-xylenol proceeds outside the cobalt complex.

Compared with chemically similar salcomines, the catalytic activity of CoB_2 chelate is substantially lower. The structural differences between these chelates should cause this behavior. The salcomines are planar (*15*), whereas the bis(alkyl-*N*-salicylideneiminato)cobalt(II) chelates are known to be tetrahedral (*16*). A disadvantageous reorganization of their ligand sphere is connected with the formation of adducts with oxygen. Low adduct concentration and slower reaction rate should be observed as a consequence.

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REFERENCES

1. Van Dort, H. M., and Geursen, H., *Rec. Trav. Chim. Pays-Bas* **86**, 520 (1967).
2. Vogt, L. H., Wirth, J. G., and Finkbeiner, H. L., *J. Org. Chem.* **34**, 273 (1969).
3. Tomaja, D. L., Vogt, L. H., and Wirth, J. G., *J. Org. Chem.* **35**, 2029 (1970).
4. Matsuura, T., Watanabe, K., and Nishikawa, A., *Chem. Commun.* 163 (1970).
5. Tada, M., and Katsu, T., *Bull. Chem. Soc. Japan* **45**, 2558 (1972).
6. Omura, Y., Nakamura, M., Oka, M., Fujiwara, Y., and Itoi, K., *Japan Kokai* **74**, 127, 937 (1974) (C. A. **82**, 170383).
7. Kothari, V. M., and Tazuma, J. J., *J. Catal.* **41**, 180 (1976).
8. Betts, A. T., and Uri, N., *Makromol. Chem.* **95**, 22 (1966).
9. Charles, R. G., *J. Org. Chem.* **22**, 677 (1957).
10. Barrales-Rienda, J. M., and Pepper, D. C., *Eur. Polymer J.* **3**, 535 (1967).
11. Bayston, J. H., King, N. K., Looney, F. D., and Winfield, M. E., *J. Amer. Chem. Soc.* **91**, 2775 (1969).
12. Misono, A., and Koda, S., *Bull. Chem. Soc. Japan* **42**, 3048 (1969).
13. Tkáč, A., Veselý, K., and Omelka, L., *J. Phys. Chem.* **75**, 2575, 2580 (1971).
14. Tsuruya, S., Kishikawa, Y., Tanaka, R., and Kuse, T., *J. Catal.* **49**, 254 (1977).
15. Martell, A. E., and Calvin, M., "Chemistry of the Metal Chelate Compounds," Prentice Hall, New York, 1956.
16. Sacconi, L., Ciampolini, M., Maggio, F., and Cavasino, F. P., *J. Amer. Chem. Soc.* **84**, 3246 (1962).