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THE EFFICIENT CATALYSIS OF THE AUTOXIDATION OF THIOPHENOL BY A TETRADEHYDROCORRINATOCOBALT(III) COMPLEX[†]

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The oxidation of thiophenol was effectively catalyzed by dicyano-8,12-diethyl-1,2,3,7,13,17,18,19-octamethyltetradehydrocorrinatocobalt(III) ($(CN)_2Co(III)TDHC$) in methanol containing small amounts of acetic acid and sodium cyanide at room temperature. The reaction was consistent with the sequence: (1) $(CN)_2Co(III)TDHC$ is reduced to Co(I) with thiophenol without participation of molecular oxygen; (2) the Co(I) species is oxidized to Co(II)TDHC by oxygen and acid; (3) the Co(II) species is oxidized to $(CN)_2Co(III)TDHC$ by the cooperation of oxygen and cyanide ion. The Co(III) species was repeatedly used at a rate of 3-5 cycle per second as an electron transport mediator.

The redox properties of metal complexes of tetradehydrocorrins have recently attracted much attention[1-3] in reference to the catalytic functions of naturally occurring metal corrinoids and porphyrins. We report here a profound catalytic function demonstrated by dicyano-8,12-diethyl-1,2,3,7,13,17,18,19-octamethyltetradehydrocorrinatocobalt(III) ($(CN)_2Co(III)TDHC$ hereafter, **1**) in the oxidation of thiophenol.

The addition of thiophenol (150 mg) in a dilute solution of $(CN)_2Co(III)TDHC$ (5.2×10^{-6}M) in methanol (10 ml) containing acetic acid (20 mg) and sodium cyanide (2 mg) resulted in a color change from olive-green to reddish purple at room temperature. The reaction mixture showed an identical visible spectrum with that of Co(II)-TDHC (**2**). After standing at room temperature for 40 min, thiophenol was found to be completely converted to diphenyl disulfide (yield after isolation 94%) and the solution recovered its original olive-green color as its visible spectrum confirmed the regeneration of $(CN)_2Co(III)TDHC$. The thiol oxidation did not proceed to any detectable extent in the absence of $(CN)_2Co(III)TDHC$, and acetic acid or other acidic material was the indispensable cofactor for the effective catalysis by the Co(III) complex. Molecular oxygen was the stoichiometric oxidant in the catalyzed oxidation: the oxygen uptake was 0.36±0.02 mole per mole of thiophenol used (Fig. 1). Hydrogen peroxide was also produced in the course of reaction and reached its maximum accumulation (0.13 mole per mole of thiol used) at 20 min of reaction time when most of oxygen was taken up, and then gradually decreased as shown in Fig. 1. A certain amount of hydrogen peroxide thus formed directly oxidized the thiol as confirmed by

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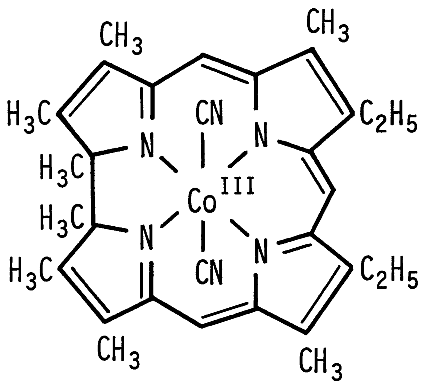

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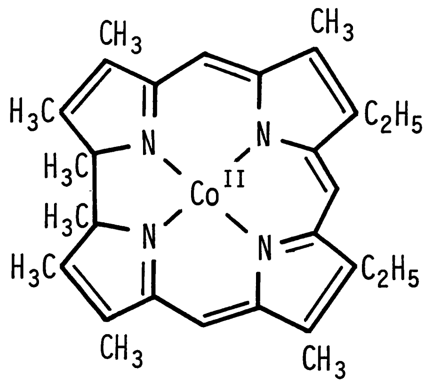

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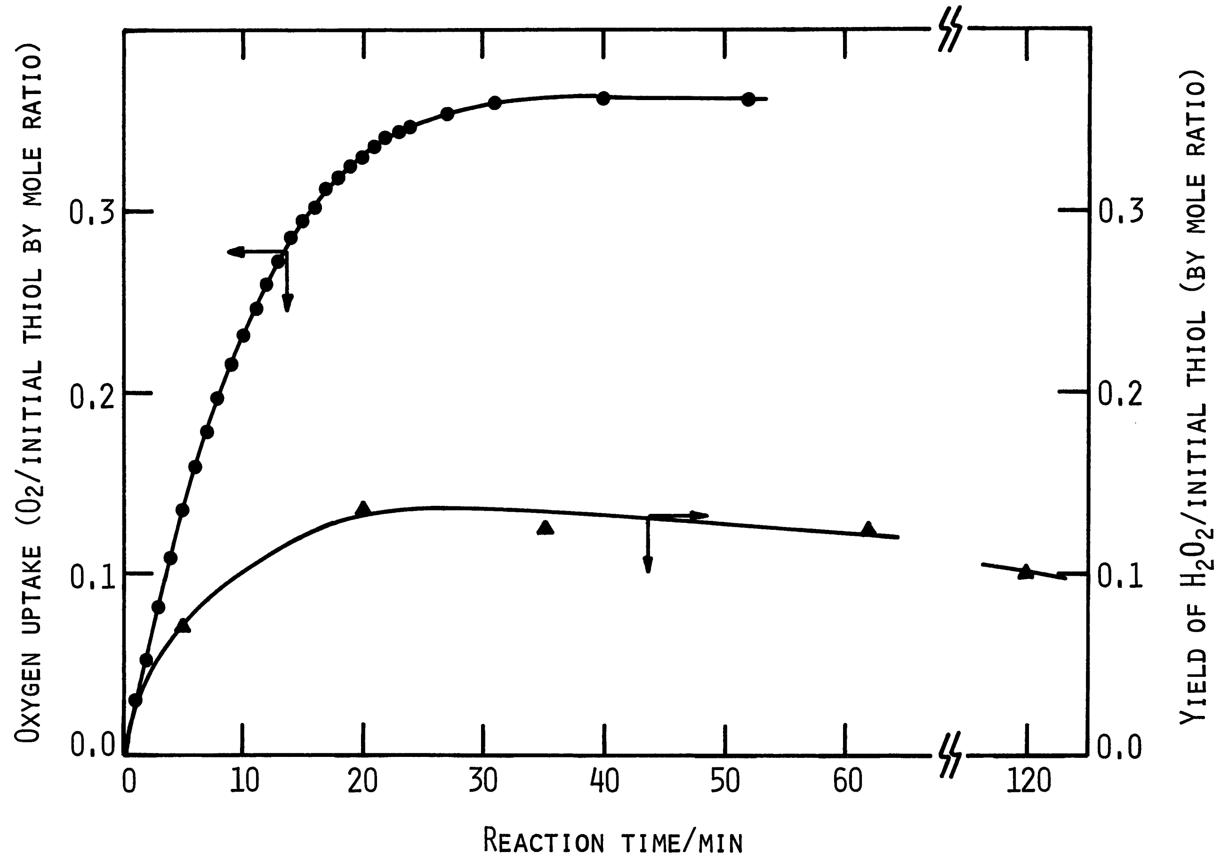


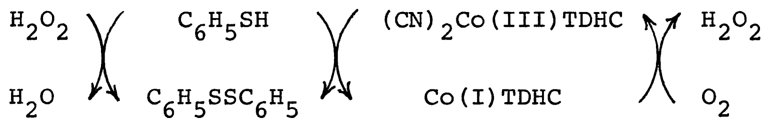
Fig. 1. Effect of $(CN)_2Co(III)TDHC$ on the oxidation of thiophenol: ●, manometrically determined oxygen uptake; ▲, iodometrically determined yield of hydrogen peroxide. Manometer contained in 3.0 ml methanol: thiophenol (0.181 mmol), $(CN)_2Co(III)TDHC$ (1.2×10^{-5} mmol), NaCN (2.9×10^{-3} mmol), and acetic acid (3.3×10^{-2} mmol). The last three components in 1.0 ml methanol were initially placed in the side arm and mixed with thiophenol in 2.0 ml methanol after 30 min of equilibration. The temperature was 25.0°C and the gas phase was air.

a separate experiment. The apparent reaction scheme consistent with the experimental results is primarily given by Eqs. (1) and (2). Under either nitrogen atmosphere or air without acetic acid, an excess amount of thiophenol reduced the cobalt(III) complex to Co(I)TDHC. The visible spectrum of the resulting solution, which was identical with that of an authentic sample of Co(I)TDHC (λ_{max}: 530 nm),[3] remained unchanged for a prolonged time and any accumulation of the disulfide was not detected. Moreover, Co(II)TDHC perchlorate failed to be reduced with the thiol to the Co(I) species. These results clearly indicate that two electrons from a pair of the thiol are first transferred to $(CN)_2Co(III)TDHC$ with concomitant formation of the disulfide, and the resulting Co(I) species is then oxidized to regenerate the Co(III) complex by oxygen with the assistance of acetic acid and cyanide ion. In support of the catalytic assistance of acetic acid, protic substances as well as proton itself have been shown to interact with various Co(I) complexes resulting in the oxidation of Co(I) to a higher oxidation state.[4] We also noted that the addition of acetic acid to an independently prepared solution of Co(I)TDHC[3] in DMF gave a spectrum identical with that of Co(II)TDHC. Thus, the reoxidation of Co(I)TDHC proceeds most plausibly through the acid catalyzed oxidation to the Co(II) species which is subsequently converted to $(CN)_2Co(III)TDHC$ as effected by the cyanide ion.

$$2C_6H_5SH + O_2 \longrightarrow C_6H_5SSC_6H_5 + H_2O_2 \qquad (1)$$

$$2C_6H_5SH + H_2O_2 \longrightarrow C_6H_5SSC_6H_5 + 2H_2O \qquad (2)$$

The rate determining step would be changed by varying the relative amounts of reacting substances involved in each redox step as well as by modifying other reaction conditions. However, the conversion of the Co(II) species to $(CN)_2Co(III)TDHC$ is most likely referred to the rate determining step under the present experimental conditions since the accumulation of the Co(II) species lasted to the very end of the catalytic oxidation as confirmed by spectroscopic means. The oxidation of thiols has been known to be subjected to catalysis by simple cobalt salts,[5] vitamin B_{12} derivatives,[6] cobalt porphyrins,[7] and other cobalt complexes.[8] However, the detailed mechanisms have not been clarified, and particularly the reduced cobalt species during catalysis have not been identified clearly for most cases possibly due to their instability. On the other hand, the present reaction sequence unambiguously consists of the following steps: (1) $(CN)_2Co(III)TDHC$ is reduced to Co(I) with thiophenol without participation of molecular oxygen; (2) the Co(I) species is oxidized to Co(II)TDHC in the subsequent step by oxygen and acid without participation of the thiol; (3) the Co(II) species is finally oxidized to $(CN)_2Co(III)TDHC$ by the cooperation of oxygen and cyanide ion. Thus, the Co(III) complex is regarded as a potential mediator for the electron transport from the thiol to the final electron acceptor, oxygen, as shown in the following scheme.



The effectiveness of the present catalytic system is attributed to its ready turnover behavior: one cycle in the cobalt valency state, *i. e.*, Co(III) → Co(I) → Co(II) → Co(III), yielded 1.4 moles of the disulfide per mole of cobalt (estimated from the amount of oxygen uptake, taking into account the direct oxidation by hydrogen peroxide as well). Consequently, the cobalt complex apparently performed turnover behavior at a rate of 3-5 cycle per second.

The critical survey of each reaction step observed in the present catalysis and the general application of $(CN)_2Co(III)TDHC$ as an electron mediator to other redox reactions are in progress in our laboratories. Such studies would provide a clue to understanding the functions of the naturally occurring electron transport catalysts, cytochromes.

REFERENCES

1) C. M. Elson, A. Hamilton, and A. W. Johnson, *J. Chem. Soc. Perkin I*, 775 (1973).

2) N. S. Hush and I. S. Woolsey, *J. Amer. Chem. Soc.*, 94, 4107 (1972).

3) Y. Murakami and Y. Aoyama, *Bull. Chem. Soc. Japan*, 49, 683 (1976).

4) A. M. Tait, M. Z. Hoffman, and E. Hayon, *J. Amer. Chem. Soc.*, 98, 86 (1976) and references therein.

5) P. C. Jocelyn, "Biochemistry of the SH Group," Academic Press, New York, N. Y. (1972), Chapter 4.

6) J. L. Peel, *Biochem. J.*, 88, 296 (1963).

7) L. D. Rollmann, *J. Amer. Chem. Soc.*, 97, 2132 (1975).

8) I. G. Dance, R. C. Conrad, and J. E. Cline, *J. Chem. Soc. Chem. Commun.*, 13 (1974).

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