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μ-Peroxobis(pentacyano)dicobaltate(III) as an Oxidizing Agent

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It has been reported by Haim and Wilmarth[1] that the pentacyanocobaltate(II) (PC-II) is oxidized with oxygen at 0°C to form μ-peroxobis(pentacyano)dicobaltate(III)(POPC), which is decomposed with sulfuric acid to produce hydrogen peroxide.

There have also been several reports concerning the direct epoxidation of acrolein with hydrogen peroxide[2] and of propylene with organic hydroperoxide[3,4] or organic peracid.[5]

Since the possibility of the epoxidation of acrolein and propylene was expected on the basis of the above reports, an attempt was made to epoxidize them with POPC, but the results obtained were negative.

The present paper deals with spectrophotometric and polarographic investigations of the chemical behaviors of POPC to clarify the reason for the negative results.

Experimental

Preparation of POPC. POPC was prepared by oxidizing PC-II with oxygen at 0°C or by dropping a cobalt(II) nitrate solution into a potassium cyanide solution under the passage of oxygen gas at the same temperature. POPC in an aqueous solution was reddish brown and precipitated as crystalline brown needles by addition of methanol. POPC was determined by treating with sulfuric acid and by titrating the hydrogen peroxide produced iodometrically. The yield reached 95.5% under the following conditions; 1150 m*l* oxygen gas/min, 0°C, 30 min (dropping time), 5 : 1 mol ratio (0.1 M Co^{2+}), and 50 m*l* total volume.

Apparatus. A Shimadzu QR-50 spectrophotometer, a Yanagimoto P-8-D polarograph, a Yanagimoto GC-220 gas chromatograph, *etc.* were used.

Results and Discussion

POPC in an aqueous solution was stable for a long time in air or nitrogen atmosphere at 0°C,

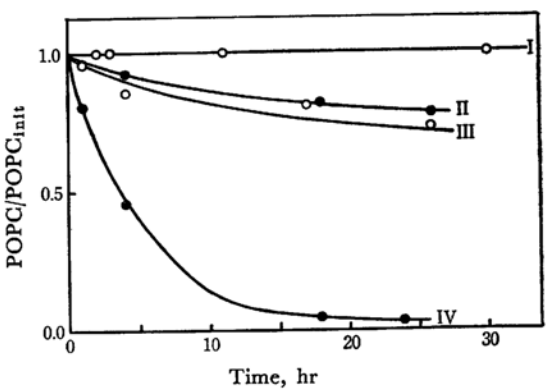

Fig. 1. Thermal stability of POPC.
I $POPC_{Init}$: 2.47×10^{-2} M, temperature: 0°C
II $POPC_{Init}$: 2.57×10^{-2} M, temperature: 25°C
III $POPC_{Init}$: 2.72×10^{-2} M, temperature: 30°C
IV $POPC_{Init}$: 2.57×10^{-2} M, temperature: 50°C

1) A. Haim and W. K. Wilmarth, *J. Am. Chem. Soc.*, **83**, 509 (1961).
2) G. B. Payne, *ibid.*, **81**, 4901 (1959).
3) J. Kollar, *Belg. Pat.* 641452 (1964).
4) Halcon International Inc., *Neth. Pat. Appl.*, 6402 137 (1964).
5) N. Ota and J. Imamura, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **69**, 1459 (1966).

but it was decomposed markedly with the rise of temperature to produce pentacyanocobaltate(III) (PC-III) (Fig. 1).

The absorption spectra of POPC, PC-II, PC-III and hexacyanocolaltate(III)(HC-III) are shown in Fig. 2. The absorption of PC-II and PC-III at 310 mμ is so small that the absorption maximum at the same wavelength is attributed to the formation of POPC. There is a linear relationship between the absorbance and the concentration of POPC which was determined by iodometry (Fig. 3).

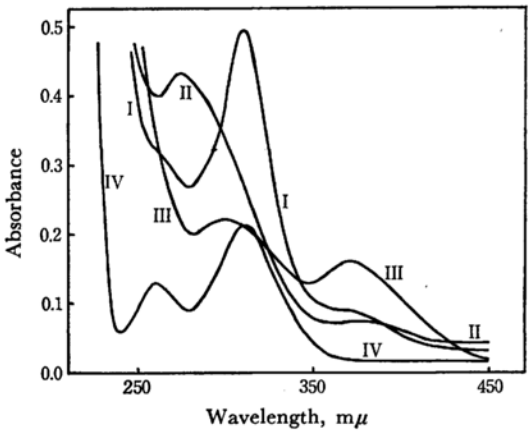

Fig. 2. Absorption spectra.
I POPC; cobalt: 2.50×10^{-4} M
II PC-II; cobalt: 2.50×10^{-4} M
III PC-III; cobalt: 1.00×10^{-3} M
IV HC-III; cobalt: 1.00×10^{-3} M
pH: 12.5, temperature: 0°C

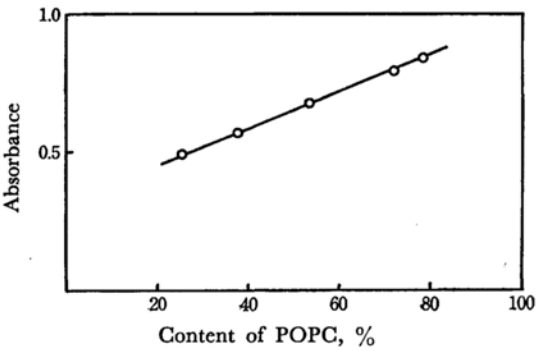

Fig. 3. Calibration curve of POPC at 0°C.
cobalt: 2.50×10^{-4} M, pH: 12.5, wavelength: 310 mμ

The following results were obtained by spectrophotometric investigation: 1) The absorption spectra of POPC solutions prepared by the above-mentioned methods are identical with each other; 2) the absorption spectra of the solutions obtained by treating POPC with sulfuric acid or by heating POPC agree not with that of PC-II but of PC-III; 3) the same absorption spectrum as that of HC-III is obtained by adding potassium cyanide to PC-III and by heating. A schematic diagram from the results is given in Fig. 4. It is easily supposed from 2) that POPC is not produced successively since an oxygen molecule can not coordinate to PC-III.

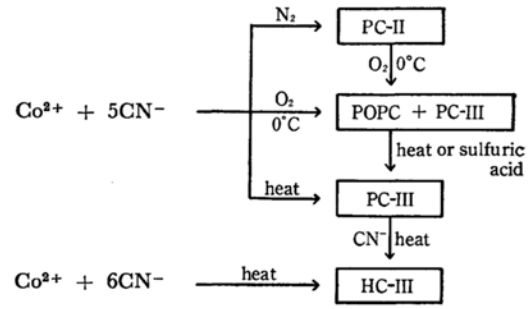

Fig. 4. The schematic diagram for cobalt cyanide complexes.

Table 1. The half wave potentials and the wave heights measured
Concentration of cobalt $=2.50\times10^{-3}$ M, pH=12.5, Temperature=0°C

		Half wave potential (V)	Wave heights (μA)
PC-III		−1.65	7.45
PC-II		−1.59	4.00
POPC	a	−1.66	8.30
	b	−1.68	10.7
O_2	1st step	−0.20	
	2nd step	−1.30	
H_2O_2		−1.19	

a, content 23%
b, content 88%

The polarographic reduction waves of POPC, PC-II, PC-III, hydrogen peroxide and oxygen were recorded with the use of a dropping mercury and saturated calomel electrode couple, and the results are shown in Table 1. As can be seen, the half wave potential of POPC is more negative than that of hydrogen peroxide in spite of the fact that POPC reacts with sulfuric acid to give hydrogen peroxide. This shows that POPC is quite different from hydrogen peroxide. Though there seemed to be two paths as the reduction mechanism of POPC and two waves were expected, only a single wave was observed. This means that the respective reactions in the two reduction paths proceed very fast.

$$\mathrm{CoOOCo} \begin{cases} \xrightarrow{2e} \mathrm{Co^{+} + O_2^{2-}} \\ \xrightarrow{e} \mathrm{Co^{3+} + OH^{-}} \end{cases} \begin{matrix} \xrightarrow{e} \\ \xrightarrow{2e} \end{matrix} \mathrm{Co^{+} + OH^{-}}$$

The wave height estimated on the basis of the above reduction mechanism and the concentration of POPC agreed well with that of POPC in a polarogram.

Epoxidation. Acrolein and propylene were treated with POPC under the conditions: pH 8—12, 1.5—30°C, and 40—180 min (reaction time).

The reaction mixtures were examined by a gas chromatograph. No epoxide was found. Acrolein was treated similarly with a solution obtained by adjusting the pH to 8—9 after acidfication of POPC solution with sulfuric acid. The gas chromatogram obtained showed a peak of glycidaldehyde.

The failure in the direct epoxidation with POPC is attributed to the inertness of POPC to olefins.