BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 2440—2442 (1968)

Catalytic Activity of Polymeric Vitamin B_{12} Model Compounds

Tadashi SASAKI and Fujinao MATSUNAGA

Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya

(Received December 11, 1967)

$[CoX(DH)_2 \cdot P\text{-}4VP]$ (X: CN, Cl)-type polymeric complexes were prepared from dimethylglyoxime (DH_2) and poly-4-vinylpyridine (P-4VP) by a procedure similar to that reported for the preparation of $[CoX(DH)_2 \cdot Pyr]$ (Pyr: pyridine) (T. Sasaki and F. Matsunaga, submitted to *Bull. Chem. Soc. Japan*). Moreover, their catalytic activities in the decomposition reaction of hydrogen peroxide were compared with those of the corresponding monomeric complexes $[CoX(DH)_2 \cdot Pyr]$; it was found that their activities decreases in the following order:

$$[CoCl(DH)_2 \cdot P\text{-}4VP] > [CoCl(DH)_2 \cdot Pyr] \gg [CoCN(DH)_2 \cdot P\text{-}4VP] > [CoCN(DH)_2 \cdot Pyr]$$

About the relationship between structure and activity, it was concluded that the activity is much influenced by the nature of the X ligand of cobaloximes. It increases with a decrease in the interaction between the cobalt and nitrogen of a pyridine ring and with a weakening in the basicity of the coordinated bases. The structures of the polymeric complexes are discussed on the basis of their spectral data.

Much attention has been paid to the syntheses and catalytic behavior of polymeric chelates and studies have been made on the basis of their reactivity being similar to that of some enzymes with the object of obtaining enzymatic models from polymeric chelates. They were expected to show a "polymer effect" in their chemical character on the one hand, and to show some specific properties as polyelectrolytes on the other.[1] Akabori *et al.*[2] have found the catalytic activity of synthesized resins involving pyridoxal and salicylaldehyde in the racemization of amino acid, and Keyer[3] has reported on the catalytic activity of polymeric chelates in the decomposition reactions of hydrazine hydrate and hydrogen peroxide, though the corresponding monomeric chelates show no activity. Hatano *et al.*[4] have also described similar catalytic activity in polymeric chelates derived from some β-diketones and copper, while Roginski[5] has discussed the relationship between the electroconductivity and the catalytic activity of Cu-phthalocyanines in the oxidation of cumene, cyclohexene, and stilbene, including the decomposition reaction of hydrazine hydrate.

In a continuation of our previous examination,[6] we carried out the syntheses of polymeric vitamin B_{12} model compounds from dimethylglyoxime and poly-4-vinylpyridine according to the previous methods[6] and measured their catalytic activities in the decomposition reaction of hydrogen peroxide in comparison with the corresponding monomeric complexes, both in heterogeneous systems. The structures of the polymeric chelates will be discussed on the basis of their infrared and far-infrared spectra in the correlation with their catalytic activities.

Experimental

Materials. All the materials used in this experiment are commercially available except for poly-4-vinylpyridine, which was prepared by the procedure described by Katchalsky.[7] This polymer was soluble in hydrochloric acid and alcohol, but not in chloroform, dimethylformamide, *n*-pentane, or boiling benzene. $\eta_{sp}=0.23$ (EtOH, 0.33 g/100 m*l* at 20°C).

Preparation of Polymeric Chelates. The polymeric chelate, $[CoCN(DH)_2 \cdot P\text{-}4VP]$, was prepared by the following scheme:

DH_2 (0.687 g, 0.0058 mol) and 0.35 g (0.0033 mol) of p-4VP were dissolved in 40 m*l* of hot 95% ethanol, and into this solution there was stirred a solution of 0.65 g (0.0028 mol) of $CoAc_2 \cdot 4H_2O$ and 0.65 g (0.0025 mol) of KCN in 10 m*l* of water. The reaction mixture was then aerated vigorously for 4 hr while it was being heated at 70—80°C. Cobalt acetate was added last to avoid any cross-linkage of P-4VP with a cobalt atom. The precipitated brown powder was then collected and washed several times with large amounts of water,

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[1] M. Hatano, *J. Synth. Org. Chem. Japan*, **24**, 453 (1966), and the references citred therein.

[2] K. Toi, Y. Izumi and S. Akabori, This Bulletin, **35**, 1422 (1962); *ibid.*, **36**, 734 (1963); K. Toi, *ibid.*, **36**, 739 (1963).

[3] N. P. Keyer, *Kinetika i Kataliz*, **2**, 509 (1961); *ibid.*, **3**, 346, 680, 691 (1962).

[4] M. Hatano, Y. Nose, T. Nozawa and S. Kambara, *Makromol. Chem.*, **98**, 136 (1966).

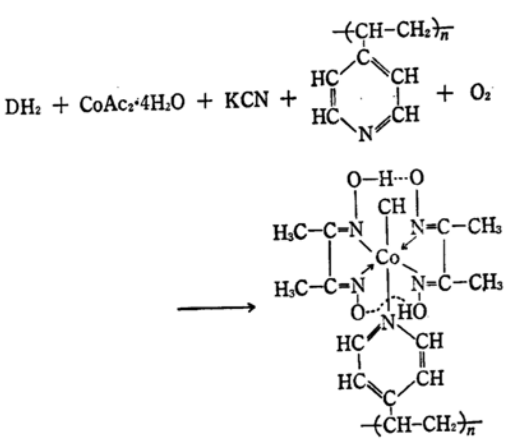
[5] S. Z. Roginski, *Doklady Akad. Nauk*, **67**, 97 (1959); *Kinetika i Kataliz*, **4**, 431 (1963).

[6] T. Sasaki and F. Matsunaga, submitted to this Bulletin.

[7] A. Katchalski, K. Rosenheck and B. Altmann, *J. Poly. Sci.*, **23**, 9055 (1957).

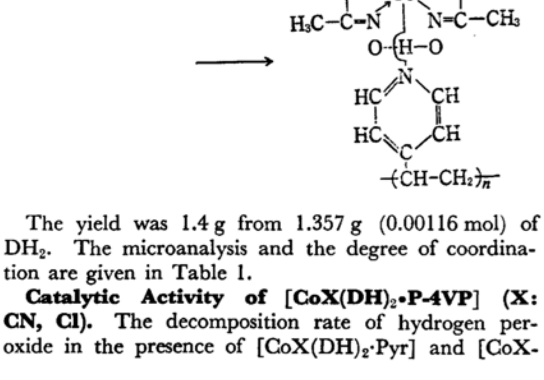
Table 1. Microanalyses and degree of chelation

Composition	Found (Calcd)				Degree of coordination
	C%	H%	N%		
$[CoCN(DH)_2 \cdot Pyr] \cdot \frac{1}{2}H_2O$	41.69 (41.56)	5.02 (5.00)	20.38 (20.84)		
$[CoCN(DH)_2 \cdot P\text{-}4VP]$	48.53 (47.74)	5.25 (5.63)	17.65 (17.65)		65%
$[CoCl(DH)_2 \cdot P\text{-}4VP]$	48.26 (48.01—49.25)	5.44 (5.21—5.18)	16.45 (15.82—15.89)	Cl: 7.82 (6.93—7.10)	84—86%
$[CoCl(DH)_2 \cdot Pyr]$	N: 17.19 (17.34)	Cl: 9.14 (8.78)			



ethanol, and ether successively and dried under a vacuum. The yield was 0.9 g, mp >300°C. The microanalysis and the degree of coordination[*1] are given in Table 1.

Similarly, a polymeric chelate, $[CoCl(DH)_2 \cdot P\text{-}4VP]$, was prepared by:



The yield was 1.4 g from 1.357 g (0.00116 mol) of DH_2. The microanalysis and the degree of coordination are given in Table 1.

Catalytic Activity of $[CoX(DH)_2 \cdot P\text{-}4VP]$ (X: CN, Cl). The decomposition rate of hydrogen peroxide in the presence of $[CoX(DH)_2 \cdot Pyr]$ and $[CoX(DH)_2 \cdot P\text{-}4VP]$ was measured at 40°C as follows: 10 m*l* of 30% aqueous hydrogen peroxide (8.8×10^{-3} mol), 10 m*l* of a phosphate buffer at pH 7.0 and a small amount of a non-ionic surface-active reagent, polyoxyethylene nonylphenol ether $\bar{P}=10$, were added to 60 m*l* of distilled water so as to bring the total volume to exactly 80 m*l*. After adding to this solution enough cobalt chelate to correspond to the 2.48×10^{-4} atom/*l* cobalt content, 5 m*l* aliquots were taken at regular time intervals, the decomposition was stopped by adding 10 m*l* of 9 N sulfuric acid, and the residual hydrogen peroxide was titrated with a 1/100 N $KMnO_4$ solution.

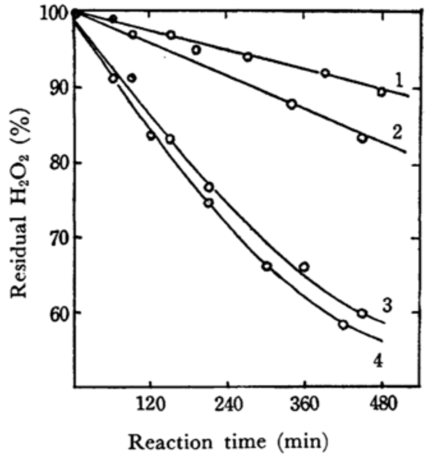


Fig. 1. Decomposition reaction of hydrogen peroxide.

Reaction temp: 40°C

Cobalt content in catalyst: 2.48×10^{-4} g atom/*l*

$[H_2O_2]_0 = 8.8 \times 10^{-3}$ mol/*l*

1 $[CoCN(DH)_2 \cdot Pyr]$

2 $[CoCN(DH)_2 \cdot P\text{-}4VP]$

3 $[CoCl(DH)_2 \cdot Pyr]$

4 $[CoCl(DH)_2 \cdot P\text{-}4VP]$

[*1] The degree of coordination means the mole percentage of the chelate per monomer unit of P-4VP; it is readily calculated from the elemental analysis—that is, 100% means C, 45.71; H, 5.00; N, 20.00% calcd. for $(C_{16}H_{21}O_4N_6Co)_n$, and 0% means C, 79.96; H, 6.71; N, 13.32% calcd. for $(C_7H_7N)_n$. The observed values are located between these two values, for example, between 45.71 and 79.96 for C, and the deviations are expressed in the degree of coordination.

TABLE 2. CHARACTERISTIC BANDS OF MONOMERIC AND POLYMERIC CHELATES (cm^{-1})

Compound	$\nu_{C\equiv N}$	$\nu_{O-H\cdots O}$	$\nu_{C=N}$	ν_{NO}	δ_{NO}	ν_{Co-N}
[CoCN(DH)$_2$·Pyr]	2155	1745	1561	1239	1091	529, 518
[CoCN(DH)$_2$·P-4VP]	2155	1740	1563	1240	1095	529, 518
[CoCl(DH)$_2$·Pyr]		1740	1561	1239	1090	518
[CoCl(DH)$_2$·P-4VP]		1740	1562	1240	1095	518

The results are summarized in Fig. 1. When, in the above experiment, a mixture of P-4VP and DH$_2$ was used instead of [CoX(DH)$_2$·P-4VP], no activity was observed.

p*K* Values of the Coordinated Pyridine. The p*K*' values of pyridine and P-4VP were obtained from their titration curves. Because P-4VP was insoluble in water, P-4VP was previously dissolved in dilute hydrochloric acid of a known concentration, and this solution was titrated with 0.01 N NaOH. As NaOH was added to the solution, P-4VP was precipitated.

Infrared and Far-infrared Spectra. The infrared spectra of the chelates were measured in KBr pellets with a JASCO recording infrared spectrophotometer, Model IR-S, while the far-infrared spectra were measured with a Perkin-Elmer grating infrared spectrophotometer, Model 337.

Results and Discussion

Structural Elucidation of Polymeric Chelates. For this purpose, the infrared and far-infrared spectra of polymeric chelates were investigated and compared with the corresponding monomeric chelates. As is shown in Tables 2 and 3, the general patterns of the polymeric chelates were similar to those of the monomeric chelates except for the absorption due to the $\nu_{C=C,\ C=N}$ of a pyridine ring, which was observed to be shifted to a somewhat higher wave number by the coordination with a cobalt atom, presumably because of a lowering of the pyridine-ring conjugation.

The p*K*' values of pyridine and P-4 VP were given as 5.03 and 3.44 respectively at 20°C from their titration curves. Brown[8] has reported an increase in the basicity of pyridine derivatives upon the introduction of an alkyl group at the 4-position of the pyridine ring, but the fact that the basicity of P-4VP was less than that of pyridine can be explained by the prohibition of a proton attack on a pyridine ring caused by electrostatic repulsion by the positive-charged pyridinium ion structure in the polymer chain, an idea of which is supported by the above infrared spectral results.

TABLE 3. CHANGE OF FREQUENCY DUE TO PYRIDINE RING DOUBLE BOND (cm^{-1})

Compound	$\nu_{C=C,C=N}$	$\Delta\nu_{C=C,C=N}$*
[CoCN(DH)$_2$·Pyr]	1609	29
[CoCN(DH)$_2$·P-4VP]	1617	17
[CoCl(DH)$_2$·Pyr]	1609	29
[CoCl(DH)$_2$·P-4VP]	1616	16
Pyr	1580	
P-4VP	1600	

* Shifts by the coordination with a cobalt atom, for example: 1609−1580=29 and 1617−1600 =17

Relationship between Catalytic Activity and Structure. As may be clearly seen from Fig. 1, the fact that chlorocarboximatocobalt(III) showed a stronger activity than cyanocarboximatocobalt(III) in both monomeric and polymeric chelates indicates that the catalytic activity is much influenced by the X ligand and that there may be some relationship between the activity and the electronic state of the chelates. Since the characteristic absorption due to ν_{Co-N} in the far-infrared region is the same in monomeric and polymeric chelates, as Table 2 shows, their bond distances are thought to remain constant. The 29 cm^{-1} higher-frequency shift between [CoX(DH)$_2$·Pyr] and pyridine is bigger than the 16—17 cm^{-1} shift between [CoX(DH)$_2$·P-4VP] and P-4VP, indicating that the catalytic activity increased with a decrease in the interaction between a cobalt and a nitrogen atom of the pyridine ring. This result can be explained also on the basis of electronic theory: the electron-withdrawing cyano group enriches the positive charge on the cobalt atom, resulting in a stronger Co–N interaction and making the catalytic activity weaker than that of the corresponding chlorocomplexes; the reverse reasoning can be applied to an electron-donating chlorine group. About the relation between the p*K* values and the catalytic activities, it can be tentatively concluded that the weaker the coordinate base, the stronger the catalytic activity becomes, as is shown by a comparison of activity between polymeric and monomeric chelates, though further studies using several monomeric catalysts with known p*K* values are necessary to confirm this relation.

The authors wish to thank the Takeda Research Foundation for its financial support.

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[8] H. C. Borwn and X. R. Mihm, *J. Am. Chem. Soc.*, **78**, 1723 (1956).