

point and X-ray diffraction pattern. Concentration of the methanol used for trituration gave a syrup which furnished the methylphenylhydrazone of D-talose.

A sample of the 0.5 *N* acid hydrolysate of hygromycin B was subjected to paper chromatography using pyridine-ethyl acetate (2:5) saturated with water as the moving phase. The only reducing sugar found to be present had an R_f value identical with that of D-talose.

THE LILLY RESEARCH LABORATORIES
ELI LILLY AND COMPANY
INDIANAPOLIS 6, INDIANA

PAUL F. WILEY
MAX V. SIGAL, JR.

RECEIVED JANUARY 23, 1958

PEROXODICOBALT(III) COMPLEXES,
INTERMEDIATES IN THE CATALYTIC
DECOMPOSITION OF HYDROGEN PEROXIDE

Sir:

Cobalt(II) complexes of neutral amino acids are only slowly oxidized by oxygen.¹ However, they catalyze the decomposition of hydrogen peroxide and, at the same time, they are rapidly oxidized to stable red-violet cobalt(III) complexes.^{2,3} We have also observed the transient appearance of amber and red solutions. The similarity of the amber colors to those of solutions of peroxodicobalt(III) complexes⁴ prompted this investigation of the reaction between hydrogen peroxide and the cobalt(II) complexes of the glycinate ion.

The stable red-violet solutions contain an equilibrium mixture of *cis* and *trans*-hydroaquoobis-(glycinate)-cobalt(III). Identical solutions are obtained by treating chloraquoobis-(glycinate)-cobalt(III) with silver oxide. These solutions were separated into two fractions by means of a cation-exchange resin and the two fractions were identified by comparing their absorption spectra with those of *cis*- and *trans*-hydroaquoobis-(ethylenediamine)-cobalt(III) at 0°. The assignment of the *cis* and *trans* configurations is also in agreement with *trans* effect on the strength of diaquo acids.⁵

The color of the transient red solutions is due to the *trans*-cobalt(III) complex which undergoes an intramolecular rearrangement to form the red-violet equilibrium mixtures. Spectrophotometric studies showed that the amber solutions contained

the *trans* complex, which is formed by the direct action of hydrogen peroxide on cobalt(II) glycinate, and an unstable yellow-brown substance. After correcting for the presence of the *trans* complex, the absorption spectrum of the yellow-brown material was found to be nearly identical to that of tetrakis-(glycylglycinate)- μ -peroxodicobalt(III)⁶ in both visible and ultraviolet regions (no max. or min.). The corresponding compounds of valine and leucine can be extracted into butanol, indicating a neutral molecule.

The formation of a peroxo complex is indicated by the evolution of oxygen from the catalase treated amber solutions upon the addition of potassium triiodide,⁷ acidification or standing. Using manometric methods the rate constant for the decomposition of the peroxo complex was found to be $9 \times 10^{-3} \text{ min.}^{-1}$ at 0°.

The formation of a peroxo complex is also shown by the reduction of the catalase treated amber solutions at the dropping mercury electrode. Half-waves were observed at -0.11, -0.96 and -1.48 volts *vs.* S.C.E. The first wave is due to the reduction of cobalt(III) while the second is due to the reduction of liberated hydrogen peroxide. The second wave is broad and disappears as the amber solutions turn red. The rate constant for the simultaneous decrease in the diffusion current is $7.5 \times 10^{-3} \text{ min.}^{-1}$ at 0°.

Although several reactions may be responsible for the decomposition of hydrogen peroxide by the cobalt(II) glycinate ion, a satisfactory mechanism should include the formation and decomposition of a peroxodicobalt(III) complex, probably diaquotetrakis-(glycinate)- μ -peroxodicobalt(III). The decomposition of the hydrogen peroxide soon stops because of the simultaneous formation of *trans*-hydroaquoobis-(glycinate)-cobalt(III), a stable complex. The results of a more detailed study will be reported in a later publication. Future investigations include a study of the mechanisms of the formation of the peroxo complexes.

The authors wish to thank the Fels Foundation and the Kettering Foundation for the use of the Warburg Apparatus and Sargent Model XXI Polarograph, respectively. This work was supported by a grant from the National Institutes of Health (PHS).

DEPARTMENT OF CHEMISTRY
ANTIOCH COLLEGE
YELLOW SPRINGS, OHIO

RICHARD G. YALMAN
MARGARET B. WARGA

RECEIVED DECEMBER 7, 1957

- (1) H. Ley and H. Winkler, *Ber.* **42**, 3894 (1909); **45**, 372 (1912).
(2) J. Hearon, D. Burk and A. L. Schoole, *J. Nat. Cancer Inst.*, **9**, 337 (1949).
(3) V. I. Avvakumov and G. A. Dobren'kov, *Trudy Kazan. Khim. Technol. Inst. im S. M. Kirova*, **19-20**, 229 (1954-55).
(4) L. Michaelis, *Federation Proc.*, **7**, 509 (1948).
(5) J. Bjerrum and L. Rasmussen, *Acta Chem. Scand.*, **6**, 1265 (1952).

- (6) C. Tanford, D. C. Kirk, Jr., and M. K. Chantooni, Jr., *THIS JOURNAL*, **76**, 5325 (1954).
(7) R. G. Yalman, *Anal. Chem.*, **28**, 91 (1956).