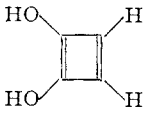
that the complex $Fe_2C_{10}H_4O_8$, formed[10,11] by the interaction of acetylene with an alkaline solution of iron carbonyl anion, contains a four-carbon chain. The experimental evidence presented[9] is equally compatible with the presence of a cyclobutadiene ring such as



analogous to that proposed for $(CH{\equiv}CH)_2Fe(CO)_3$[1]

The principle of carbon skeleton synthesis during complex formation offers a new route to the formation of organic compounds which may have practical value in synthetic organic chemistry. Indeed, we succeeded in synthesizing durohydroquinone without isolation of an intermediate complex by merely adding methanolic HCl to the mixture of dimethylacetylene and $Fe(CO)_5$ during irradiation.

A complex similar to I may conceivably be an intermediate in Reppe's synthesis of hydroquinone from iron pentacarbonyl and acetylene at elevated pressure and temperature.[10]

(10) W. Reppe and H. Vetter, *Ann. Chem. Justus Liebig*, **582**, 133 (1953).

(11) H. W. Sternberg, R. A. Friedel, R. Markby and I. Wender, THIS JOURNAL, **78**, 3621 (1956).

CENTRAL EXPERIMENT STATION HEINZ W. STERNBERG
BUREAU OF MINES RAYMOND MARKBY
PITTSBURGH, PA. IRVING WENDER

RECEIVED JANUARY 24, 1958

A CRYSTALLINE PENTAPOLYPHOSPHATE

Sir:

In the sodium[1] and potassium[2] phosphate systems, the largest chain oligophosphate which appears in the phase diagram is the tripolyphosphate. Because of this, there was considerable discussion in the scientific literature of the 40's that higher members of the homologous series of chain phosphates, such as the tetra- and pentapolyphosphates, do not exist. This notion has, of course, been disproved by modern tools such as ion exchange and paper chromatography.[3] Nevertheless, it is of considerable interest to point out here that pentapolyphosphate appears as a crystalline entity in a phase diagram.

In 1955, it was shown[4] that a crystalline salt of the composition $3PbO{\cdot}2P_2O_5$ appeared in the lead phosphate phase diagram. Paper chromatographic studies[5] in this Laboratory demonstrated that this compound and a similar barium compound were truly tetrapolyphosphates. We have now found that the crystalline calcium phosphate called trömelite which appears in the calcium phosphate phase diagram[6] is a pentapolyphosphate—the anion of which consists of a chain of five phosphorus atoms alternating with oxygen atoms. This has been demonstrated by paper chromatography[3] of solutions made by dissolving the trömelite in various solutions containing ethylenediaminetetraacetate. These results will be reported in detail, along with data on the molecular constitution of the other crystalline calcium phosphates, in a forthcoming paper to be submitted to This Journal.

(1) E. P. Partridge, V. Hicks and G. V. Smith, THIS JOURNAL, **63**, 454 (1941); G. W. Morey and E. Ingerson, *Am. J. Sci.*, **242**, 1 (1944).

(2) G. W. Morey, THIS JOURNAL, **76**, 4724 (1954); G. W. Morey, F. R. Boyd, J. R. England and W. C. Chen, *ibid.*, **77**, 5003 (1955).

(3) *E.g.*, E. Karl-Kroupa, *Anal. Chem.*, **28**, 1091 (1956).

(4) R. K. Osterheld and R. P. Langguth, *J. Phys. Chem.*, **59**, 76 (1955).

(5) R. P. Langguth, R. K. Osterheld and E. Karl-Kroupa, *ibid.*, **60**, 1335 (1956).

(6) W. L. Hill, G. F. Faust and D. S. Reynolds, *Am. J. Sci.*, **242**, 457 (1944).

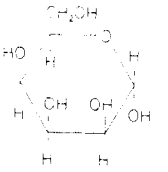
INORGANIC CHEMICALS DIVISION
RESEARCH DEPARTMENT JOHN R. VAN WAZER
MONSANTO CHEMICAL COMPANY
ST. LOUIS 24, MISSOURI SHIGERU OHASHI

RECEIVED JANUARY 8, 1958

ISOLATION OF D-TALOSE FROM A NATURAL SOURCE

Sir:

Although D-talose (I) has been well-known for many years, it has not been isolated previously from natural sources. This communication reports the isolation of D-talose from the antibiotic, hygromycin B.[1] The antibiotic was hydrolyzed with 0.5 *N* sulfuric acid, and the sulfate was removed as barium sulfate. The resulting solution was passed over IR-120, and the effluent was concentrated to dryness under reduced pressure. The residue was triturated twice with methanol. The methanolic solution thus obtained yielded crystalline D-talose. The crude talose was purified by crystallization of the impurities from water, concentration of the aqueous, trituration of the residue with methanol and again crystallizing from the methanolic extract. The crystals thus formed had the following properties: m.p. 128–132°; $[\alpha]^{26}D$ +16.9° at equilibrium (*c* 1, H_2O). *Anal.* Calcd. for $C_6H_{12}O_6$: C, 39.99; H, 6.72; mol. wt., 180. Found: 39.96; H, 6.92; mol. wt. (crystallographic), 178. Melting points reported for α-D-talose are 133–134°,[2] 130–135°,[3] and 127–129°.[4] Reported rotations are, after mutarotation, +20.8°,[2] +19.7°,[3] and +20.6°.[4] Comparison of the product isolated from hygromycin B with synthetic α-D-talose[5] by means of X-ray diffraction patterns and paper chromatography indicated that the two were identical. The methylphenylhydrazone of the natural D-talose was prepared according to the procedure of Levene and Tipson.[3] This derivative melted at 153–154° (lit.[3] 154°) and upon admixture with an authentic sample showed no depression in melting point. The X-ray diffraction pattern of the derivative from natural material was identical with that from synthetic material.



More D-talose was obtained by concentration of the filtrate after removal of the first crop of crystalline material and trituration of the residue with methanol. This material was identified by melting

(1) R. L. Mann and W. W. Bromer, THIS JOURNAL, **80**, May (1958).

(2) W. W. Pigman and H. S. Isbell, *J. Research Natl. Bur. Standards*, **19**, 189 (1937).

(3) P. A. Levene and R. S. Tipson, *J. Biol. Chem.*, **93**, 631 (1931).

(4) W. Bosshard, *Helv. Chim. Acta*, **18**, 482 (1935).

(5) Supplied by General Biochemicals, Inc.

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 — PAUL F. WILEY
INDIANAPOLIS 6, INDIANA — 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) complexes[4] 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*-hydroaquobis-(glycinate)-cobalt(III). Identical solutions are obtained by treating chloraquobis-(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*-hydroxoaquobis-(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 9×10^{-3} 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 7.5×10^{-3} 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*-hydroxoaquobis-(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.

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DEPARTMENT OF CHEMISTRY
ANTIOCH COLLEGE — RICHARD G. YALMAN
YELLOW SPRINGS, OHIO — MARGARET B. WARGA

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(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. Chantoont, Jr., THIS JOURNAL, **76**, 5325 (1954).
(7) R. G. Yalman, *Anal. Chem.*, **28**, 91 (1956).