to C5P which was isolated by cation-exchange chromatography.[7]

Evidence for the source of the amino group was obtained by carrying out the reaction with $N^{15}H_3$.[8] CTP, ATP and UTP were separated by anion-exchange chromatography. The cytosine nucleotide was freed of contaminating UDP by hydrolysis to C5P which was isolated by cation-exchange chromatography.[7] Analysis of the nitrogen derived from the isolated nucleotides after Kjeldahl digestion yielded the following results, expressed in atom per cent. excess: amino N of CTP, 17.3; ATP, 0.00; and UTP, 0.00. The $NH_3$ in the reaction mixture at zero time contained 17.5 atom per cent. excess $N^{15}$. With enzyme fraction IV, D,L-aspartate, D,L-glutamate (each 0.02 *M*), L-asparagine, L-glutamine (each 0.01 *M*), and glycine (0.10 *M*) were incapable of satisfying the $NH_3$ requirement. $NH_2OH$, on the other hand, could replace $NH_3$ and two new compounds were formed which could be distinguished from the cytosine nucleotides on the basis of their chromatographic properties on anion-exchange resin, their spectrum (peak at 280 mμ, 280/260 = 1.77, 290/280 = 0.84, at *p*H 2), and their ability to yield color with $FeCl_3$. They have been tentatively identified as N–OH–CTP and N–OH–CDP.

Inorganic phosphate release accompanying CTP formation was studied with ATP labeled with $P^{32}$ in the two terminal phosphate groups. In three experiments the synthesis of 0.044, 0.069, and 0.034 μmole of cytidine nucleotide was accompanied by the release of 0.045, 0.066, and 0.032 μmole of Pi from ATP, respectively. No detectable amination of glutamate or ITP occurred with the partially purified enzyme.

(7) W. E. Cohn, *Science*, **109**, 377 (1949).

(8) $N^{15}$ determinations were carried out by Mrs. G. Shearer, Department of Botany, Washington University, under the supervision of Dr. B. Commoner.

DEPARTMENT OF MICROBIOLOGY
WASHINGTON UNIVERSITY SCHOOL OF MEDICINE
ST. LOUIS, MISSOURI IRVING LIEBERMAN

RECEIVED FEBRUARY 16, 1955

## STRUCTURE AND SYNTHESIS OF KINETIN[1]

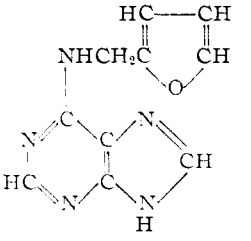
*Sir:*

Hydrolysis of kinetin, a recently isolated cell division factor,[2] in 2*N* HCl or $H_2SO_4$ at 120° for two hours caused a shift of its ultraviolet spectrum to one characteristic of adenine. After exhaustive ether extraction of the hydrolysis mixture, picric acid was added to the aqueous layer and a small yield of an insoluble picrate, m.p. 292–294°, resulted. The product was not well crystallized and was difficult to purify. Mixed with known adenine picrate, m.p. 298–299°,[3] it melted at 291–293°. Additional evidence for the presence of adenine was obtained by column chromatography on Dowex 50. The 260 mμ-absorbing material was eluted by 6*N*, but not by weaker, HCl, and behaved exactly as adenine does on this column.[4] Likewise the degradation product showed a single ultraviolet-quenching spot with the same $R_f$ value as authentic adenine on paper chromatograms run in three different solvent systems.

The ether extract from acid-hydrolyzed kinetin was treated with 2,4-dinitrophenylhydrazine, and the amorphous product subjected to paper chromatography in a *n*-butanol–3% aqueous ammonia system. A single spot of the same yellow color and $R_f$ value as that of authentic levulinic acid 2,4-dinitrophenylhydrazone was observed. The yield of this degradation product was also low, and the derivative proved difficult to crystallize. In the Dische test[5,6] kinetin gave a colored product with the same spectrum as that from adenine deoxyriboside, but in only 12% as great an amount.

The $pKa_1$ and $pKa_2$ values of kinetin in aqueous solution as determined by spectrophotometric methods were found to lie close to 4 and 10, respectively, and a solution of the factor in 0.05 *N* $H_2SO_4$ gave an immediate heavy white precipitate with aqueous silver nitrate. The 9-position in the adenine moiety was, therefore, not substituted. Since repeated attempts at acetylation under various conditions led in every case to recovery of unchanged kinetin, it seemed probable that no free hydroxyl or amino group was present in the molecule. Kinetin showed no optical rotation in *N* $H_2SO_4$ solution (*c*, 1.8), and zero carbon methyl by the Kuhn–Roth method.[7]

From the above and previously published[2] evidence it was concluded that kinetin most probably is 6-furfurylaminopurine, I:



Kinetin, I

This structure accounts for the analytical data and degradation products obtained and also for the marked chemical stability of kinetin.

The correctness of this structure has now been verified by synthesis of I from furfurylamine[8] and 6-methylmercaptopurine[9] by the general method of Hitchings, *et al.*[10] The crude product, in 62% yield, was recrystallized from absolute ethanol, m.p. 266–267° (sealed tube); mixed m.p. with isolated kinetin, 266–267°. The infrared and ultraviolet spectra, Dische color test, and paper chromato-

(1) This work was supported in part by research grants from the American Cancer Society, the National Science Foundation, and the Wisconsin Alumni Research Foundation.

(2) C. O. Miller, F. Skoog, M. H. Von Saltza, and F. M. Strong, THIS JOURNAL, **77**, 1392 (1955).

(3) H. B. Vickery and C. S. Leavenworth, *J. Biol. Chem.*, **63**, 579 (1925). Melting points of this derivative were taken as described by Vickery.

(4) J. S. Wall, *Anal. Chem.*, **25**, 950 (1953).

(5) Z. Dische, *Proc. Soc. Exp. Biol. Med.*, **55**, 217 (1944).

(6) P. K. Stumpf, *J. Biol. Chem.*, **169**, 367 (1947).

(7) Microanalysis by Huffman Microanalytical Laboratories, Wheatridge, Colorado.

(8) Kindly provided by F. N. Peters, Quaker Oats Company.

(9) 6-Mercaptopurine kindly provided by G. H. Hitchings, Wellcome Research Laboratories.

(10) G. B. Elion, E. Burgi and G. H. Hitchings, THIS JOURNAL, **74**, 411 (1952).

graphic behavior of the synthetic and isolated substances were identical. Tests of the biological activity of synthetic kinetin are in progress.[11]

(11) NOTE ADDED IN PROOF.—The biological activity of synthetic kinetin now has been found to be the same as that of the isolated substance in tests on tobacco tissues.

CONTRIBUTION FROM THE DEPARTMENT OF BOTANY AND DEPARTMENT OF BIOCHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN
CARLOS O. MILLER
FOLKE SKOOG
FRANCIS SHIGEO OKUMURA
MALCOLM H. VON SALTZA
F. M. STRONG

RECEIVED MARCH 30, 1955

## SELF-EXCHANGE OF BORON IN BORON HYDRIDES

*Sir:*

The considerable interest in the reaction kinetics[1-3] and in the structures of the boron hydrides[4] has prompted us to investigate the self-exchange of boron in various boron hydrides.

We have found that the exchange of boron between isotopically-normal diborane and $B^{10}$-enriched diborane is quite rapid at 25°, the rate being similar in magnitude to that observed for the deuterium exchange between diborane and hexadeuteriodiborane.[3] In contrast, we have found that no boron exchange occurs between isotopically-normal pentaborane and $B^{10}$-enriched pentaborane at temperatures up to 100° in the liquid phase or up to 250° in the gas phase. At the latter temperature the pentaborane undergoes considerable decomposition to give hydrogen and non-volatile solids (no volatile boron hydrides could be detected). It should be noted that hydrogen exchange between deuteropentaborane and pentaborane has been observed at 200°, but not at room temperature. The reactions have been followed by mass spectrometric analysis.[5] $B^{10}$-enriched diborane is prepared from $B^{10}F_3$[6] in the conventional manner[7] and $B^{10}$-enriched pentaborane is obtained by pyrolysis of the diborane.[8]

The rapid exchange of boron in diborane is consistent with the accepted diborane structure of two borines held together by two bridge hydrogens[9] and with the widely accepted reaction mechanism involving diborane dissociation.[1-3] It is interesting that pentaborane, with a pyramidal structure[10] involving direct B–B linkages, does not undergo boron exchange even under conditions which bring about copious decomposition. It is concluded that dissociation fragments do not exist in pentaborane under ambient conditions. However, the hydrogen atoms appear to be sufficiently labile at elevated temperatures for self-exchange.

This study of the self-exchange of boron, as well as that of hydrogen, is being extended to cover all known boron hydrides.

(1) R. P. Clarke and R. N. Pease, THIS JOURNAL, **73**, 2132 (1951); J. K. Bragg, L. V. McCarty and F. J. Norton, *ibid.*, **73**, 2134 (1951).

(2) S. H. Bauer, A. Shepp and R. E. McCoy, *ibid.*, **75**, 1003 (1953); H. G. Weiss and I. Shapiro, *ibid.*, **75**, 1221 (1953); A. T. Whatley and R. N. Pease, *ibid.*, **76**, 1997 (1954).

(3) P. C. Maybury and W. S. Koski, *J. Chem. Phys.*, **21**, 742 (1953).

(4) W. H. Eberhardt, B. Crawford, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 989 (1954); J. R. Platt, *ibid.*, **22**, 1033 (1954).

(5) A Consolidated model 21-103 mass spectrometer operating at 70 volts was used in this study.

(6) The $CaF_2 \cdot B^{10}F_3$ complex, obtained by allocation from the Atomic Energy Commission, Oak Ridge, Tenn., is heated to 250° *in vacuo* to release $B^{10}F_3$, which is then condensed in anhydrous ethyl ether.

(7) I. Shapiro, H. G. Weiss, M. Schmich, S. Skolnik and G. B. L. Smith, THIS JOURNAL, **74**, 901 (1952).

(8) A. B. Burg and H. I. Schlesinger, *ibid.*, **55**, 4009 (1933).

(9) W. C. Price, *J. Chem. Phys.*, **16**, 894 (1948); **15** 614 (1947).

(10) W. J. Dulmage and W. N. Lipscomb, THIS JOURNAL, **73**, 3539 (1951); K. Hedberg, M. E. Jones and V. Schomaker, *ibid.*, **73**, 3538 (1951).

RESEARCH LABORATORY
OLIN MATHIESON CHEMICAL CORPORATION
PASADENA 1, CALIFORNIA
I. SHAPIRO
B. KEILIN

RECEIVED APRIL 2, 1955

# BOOK REVIEWS

**Comprehensive Inorganic Chemistry. Volume Three. The Halogens.** By ROBERT C. BRASTED, Associate Professor of Chemistry, School of Chemistry, University of Minnesota. D. Van Nostrand Company, Inc., 250 Fourth Avenue, New York, N. Y. 1954. x + 250 pp. 16 × 24 cm. Price, $5.00.

One who examines this book may wonder just what group of readers the author is addressing. The answer is to be found in the preface which says: "Comprehensive Inorganic Chemistry is an eleven-volume reference work on the chemical elements and their inorganic compounds. It is comprehensive in the extensiveness of the fields covered rather than in the fullness of their treatment; hence, the volumes are offered individually as a ***vade mecum*** for the advanced worker—whether industrial or academic—not as an encyclopedic work. Their purpose, therefore, is to serve as a ready reference to those engaged in chemical manufacture and development and to those in advanced studies in chemistry in institutions of higher learning. . . ."

An advanced worker in inorganic halogen chemistry will be particularly interested in those portions of the book dealing with his own areas of specialization, because the point of view of the writer probably will differ from his own. He may not always agree with the author, but he probably will see new problems for research.

The author has read extensively in the recent literature on the halogens and has organized the subject matter under headings indicated by the chapter titles: (1) Fluorine, (2) Chlorine, (3) Bromine, (4) Iodine, (5) Astatine, (6) The Hydrohalides, (7) Oxycompounds of the Halogens, (8) Positive Halogens, Interhalogens and Polyhalide Anionic Complexes, (9) The Pseudohalogens (Halogenoids) and Related Compounds. Chapters 1–5 inclusive deal largely with the preparation and properties of the free elements and include discussions of many compounds with particular emphasis upon fluorides. Only a little information is given about astatine. To this reviewer the most interesting chapter is that on the oxycompounds. This is an up-to-date summary with some emphasis upon mechanism of reactions.

The book is not a text and it is not a complete reference book to the literature; it is, instead, a book on certain aspects of halogen chemistry of active interest. Even on these topics it is not a complete survey of the literature.

On the whole the book is good; however, it is not perfect. Some parts of it are so brief that they are difficult to under-