

to the synthesis of true nucleotide coenzymes was demonstrated by the following preparation of UDPG. Dicyclohexylguanidiniumuridine 5'-phosphoramidate (1 equiv.) and tri-*n*-octylammonium hydrogen glucose-1-phosphate⁶ (4 equiv.) were allowed to react for three days in dry pyridine at room temperature and the products were then separated by ion exchange chromatography. UDPG was the major ultraviolet absorbing product (66%) and was isolated readily as the amorphous dilithium salt. This material, which was homogeneous by paper and ion exchange chromatography, had uridine to phosphorus to glucose ratios of 1:1.95:1.01 and was enzymatically active.¹⁰ Its behavior to acid and alkali paralleled that reported for the naturally occurring substance.¹¹

This work is being extended to the synthesis of other nucleotide coenzymes.

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(10) H. M. Kalckar, "Methods in Enzymology," Vol. II, p. 676. Academic Press, Inc., New York, N. Y., 1955.

(11) A. C. Paladini and L. F. Leloir, *Biochem. J.*, **51**, 426 (1952).

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THE STABILITY OF POTASSIUM BOROHYDRIDE IN ALKALINE SOLUTIONS¹

Sir:

In connection with an undergraduate research program to investigate some properties of KBH_4 , it became necessary to determine its stability toward hydrolysis in alkaline solutions. It is generally stated in the literature that aqueous borohydride solutions are stable at a pH greater than 9,² but quantitative data on this point are meager. Pecsok³ has presented a study on the hydrolysis of NaBH_4 solutions buffered at various pH values between 7.7 and 9.5. Jensen⁴ has determined the stability of NaBH_4 in solutions buffered at pH 9.6 and 10.1 and of NaBH_4 dissolved in 1.00, 0.25 and 0.10 *N* sodium hydroxide.

Experimental.—0.10 *M* solutions of KBH_4 were prepared by dissolving the commercially avail-

able material⁵ in a saturated $\text{Ca}(\text{OH})_2$ solution⁶ and placed in a water-bath thermostated at $25.0 \pm 0.1^\circ$. At intervals of time, aliquot portions were analyzed for borohydride content by determining the volume of hydrogen liberated upon acidification.

Results and Discussion.⁷—A plot of the logarithm of borohydride content *vs.* time proved to be linear, indicating that the hydrolysis is first order with respect to borohydride at a constant pH . Likewise, it can be shown that Jensen's data fit the relation

$$-d(\text{BH}_4^-)/dt = k'(\text{BH}_4^-) \quad (1)$$

where k' is a function of pH .

The relation between $\log k'$ and pH is shown in Fig. 1, indicating that the reaction is also first or-

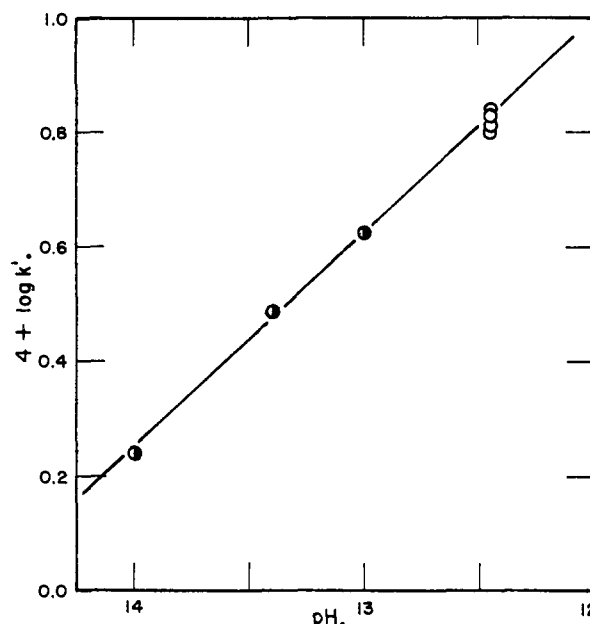


Fig. 1.—Rate constant of equation (1) as a function of pH : O, KBH_4 in $\text{Ca}(\text{OH})_2$ solutions at 25° ; ●, NaBH_4 in NaOH solutions at 24° .

der in hydronium ion. The results shown in Fig. 1 support Pecsok's conclusion that the rate of hydrolysis of borohydride solutions is controlled by the formation of $\text{HBH}_4 \cdot x\text{H}_2\text{O}$. This intermediate hydrolyzes immediately to an aquated borine radical which also hydrolyzes rapidly. It would appear from Fig. 1 that the rate of hydrolysis of the BH_4^- ion at any given pH is independent of the presence of Na^+ , K^+ , or Ca^{++} cations.

Extrapolation of the line of Fig. 1 to lower pH values does not fit the data of Jensen or of Pecsok for the hydrolytic stability of the borohydride ion in buffered solutions. Nor do Jensen's data with the borate buffer lie on the same line as do Pecsok's

(1) This investigation was supported by a grant from the Denison University Research Foundation.

(2) H. I. Schlesinger, *et al.*, *THIS JOURNAL*, **75**, 215 (1953); H. R. Hoekstra, *A.E.C.D.* 2144 (June 1947).

(3) R. L. Pecsok, *THIS JOURNAL*, **75**, 2862 (1953).

(4) E. H. Jensen, "A Study on Sodium Borohydride with Special Reference to its Analytical Application in Organic Chemistry," *Nyt Fordisk Forlag, Arnold Busch, Copenhagen*, 1954, pp. 38-48.

(5) Metal Hydrides, Inc., Beverly, Mass., Lot No. K-12, Purity 97+%.

(6) Saturated $\text{Ca}(\text{OH})_2$ at 25° has a pH of 12.45 and has been recommended as a buffer solution for defining the National Bureau of Standards standard pH scale; R. G. Bates, V. E. Bower and E. R. Smith, *J. Research Natl. Bur. Standards*, **56**, 305 (1956).

(7) More complete details will soon be published in *J. Sci. Labs., Denison Univ.*

data for pyrophosphate buffer. This would indicate that the rate of hydrolysis is influenced by the presence of different anions, which is contrary to the conclusion of Hoekstra² that, in the pH range below 9, the hydrolysis is independent of the type of buffer system used.

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A NEW SYNTHESIS OF
BIS-TRIFLUOROMETHYL-PHOSPHINE,
(CF₃)₂PH¹

Sir:

Compounds of the type (R_F)₂PH are important enough to the development of fluorocarbon-phosphorus chemistry to warrant a search for new synthetic methods offering greater convenience than the previously-reported catalytic hydrogenation processes.² We have found that the method whereby P₂(CF₃)₄ is produced by shaking (CF₃)₂PI with mercury³ becomes a good source of (CF₃)₂PH if it is performed in the presence of a protic acid. Dry hydrogen chloride, technical phosphoric acid, and trifluoroacetic acid serve equally well as sources of protons, leading to 35% conversion of the (CF₃)₂PI to (CF₃)₂PH. Even small proportions of water give minor yields of (CF₃)₂PH, probably through hydrolytic formation of hydrogen iodide. When hydrogen chloride is used, some (CF₃)₂PCl is formed (but can be removed easily by treatment with water), and the remainder of the starting material is accounted for as P₂(CF₃)₄. When phosphoric acid is used the by-products include CF₃-P-O compounds, one of which has properties corresponding to the unstable (CF₃)₂PHO.

In each of these experiments, the (CF₃)₂PI was distilled from the high-vacuum system into a flask containing a large proportion of acid and mercury. The flask was closed by a stopcock, disconnected from the vacuum system, and shaken while warming to room temperature, and for 15 minutes thereafter. The volatile products were brought into the vacuum system and separated by distillation methods. The (CF₃)₂PH was identified by observation of a 760 mm. vapor tension at 2° (literature b.p. 1°) and a molecular-weight value of 170 (calcd., 170.00). The F¹⁹ nuclear magnetic resonance spectrum (obtained with the aid of Dr. Harden McConnell and Philip Bromberg at the California Institute of Technology) showed spin-spin interactions with one P³¹ and one H¹ nucleus to give a pair of doublets. The proton magnetic spectrum consisted of two groups of seven lines due to spin-spin splitting of one phosphorus nucleus and six equivalent fluorine nuclei. Quantitative data on the splittings and chemical shifts will be published elsewhere.

An insight into the course of the (CF₃)₂PI-Hg-

(1) This research was supported by the United States Air Force under Contract AF 33(616)-2743, monitored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

(2) F. W. Bennett, H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.*, 3896 (1954).

(3) F. W. Bennett, H. J. Emeléus and R. N. Haszeldine, *ibid.*, 1585 (1952).

acid reaction was obtained from an experiment in which 0.50 mmole of (CF₃)₂PI was first shaken with mercury alone to give a 95% yield of P₂(CF₃)₄. Then the non-volatile residue was treated with dry hydrogen chloride, producing an amount of (CF₃)₂PH which would account for the missing 5% of the original (CF₃)₂P groups. Thus it would appear that a phosphorus-mercury bond had been established, possibly as (CF₃)₂PHg₂I, from which one could get either (CF₃)₂PH by the action of acid or P₂(CF₃)₄ by further action of (CF₃)₂PI. It is proposed that a wide variety of new materials containing the (CF₃)₂P group might be made by shaking (CF₃)₂PI with mercury in the presence of halides of polyvalent metals or non-metals.

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IDENTIFICATION OF RUTHENIUM SPECIES IN
AQUEOUS SOLUTION

Sir:

We have used an ion-exchange technique for identifying aqueous ruthenium species. The method promises to be very useful in studies of this element where solutions usually contain a mixture of complex ions and polymers which do not equilibrate rapidly. The method will be applicable to other systems with similar characteristics.

Two experiments are performed: the first measures the ionic charge per ruthenium atom, *a*, while the second gives the net ionic charge of the species, *b*. The ratio *b/a* equals the number of ruthenium atoms per species, *i.e.*, the degree of polymerization. Using the oxidation number, the number of negatively charged groups in the complex can be inferred. If only one complexing anion is present, the stoichiometric formula of the species is fixed.

The charge per ruthenium atom is determined from the equivalents of charge with an ion-exchange resin per gram atom of ruthenium. It was convenient to use a column technique¹ because separation and concentration of the ruthenium species could be achieved simultaneously. A dilute solution of ruthenium species, primarily in the +3 oxidation state, was stirred with Dowex 50, 200-400 mesh resin in the hydrogen ion form until most of the ruthenium was taken up by the resin. This resin was added to the top of a tapered column already containing approximately one tenth as much resin in the hydrogen ion form. The column was eluted slowly with a dilute cerous perchlorate-perchloric acid solution. The cerous ion displaced most of the ruthenium species, which formed nearly pure bands as they descended. Several samples of a particular band were collected, analyzed for total ruthenium and hydrogen ion, and the spectra checked as an indication of purity. The value of *a* is equal to the molarity of hydrogen ion plus 3 times that of cerous ion in the elutant, minus the molarity of hydrogen ion in the eluted

(1) Similar in principle to that of D. A. Everest and J. E. Salmon, *J. Chem. Soc.*, 1444 (1955).