

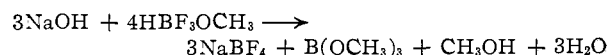
rivative melting at 225°, characteristic of normal fluoborates. This indicated the formation of sodium fluoborate. Fluorine and boron analyses further substantiated this observation.

Anal. Calcd. for NaBF₄: B, 9.85; F, 69.21. Found: B, 8.75, 9.45; F, 68.82, 69.41.

X-ray powder data for this precipitate agreed with similar data for known sodium fluoborate.

In a quantitative study of the reaction between sodium hydroxide and methoxyfluoboric acid a 90% yield of sodium fluoborate was obtained. In a typical experiment 0.0526 mole of sodium hydroxide reacted with 0.0702 mole of methoxyfluoboric acid, yielding 0.0474 mole of sodium fluoborate.

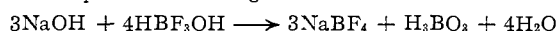
The neutralization of four moles of methoxyfluoboric acid by three moles of sodium hydroxide yields three moles of sodium fluoborate and is presumed to proceed according to the reaction



Reaction of Monohydroxyfluoboric Acid with Sodium Hydroxide.—The addition of a saturated aqueous solution of sodium hydroxide to monohydroxyfluoboric acid until the pH of the reaction mixture was about 5.5, produced boric acid. The boric acid was filtered, and identified by the X-ray powder pattern technique. Continued addition of sodium hydroxide to the filtrate from the above reaction produced sodium fluoborate, also identified by X-ray diffraction photographs.

A pH titration of monohydroxyfluoboric acid with standard sodium hydroxide exhibited two well-defined inflection points in plots of pH against ml. base. The initial inflection in the curve occurred at a pH of about 5 and corresponded to the neutralization of the acid to form sodium fluoborate and boric acid. The second inflection corresponded to the neutralization of the boric acid produced in the initial reaction. A poorly defined inflection was observed between the two points mentioned above. A proposed explanation for this curve suggests that partial hydrolysis of sodium fluoborate formed in the initial reaction required some additional base for neutralization. The shape of the entire curve is somewhat similar to that curve reported by Wamser⁷ for the titration of mixtures of fluoboric and monohydroxyfluoboric acid with sodium hydroxide. However, Wamser explained the separate inflections by assuming the formation of sodium hydroxyfluoborate and sodium fluoride in the neutralization. Neither of these products was found to be formed in the reaction of sodium hydroxide and monohydroxyfluoboric acid by the present authors.

The neutralization of four moles of monohydroxyfluoboric acid by three moles of sodium hydroxide yields three moles of sodium fluoborate and one mole of boric acid and is presumed to proceed according to the reaction



(7) C. A. Wamser, *THIS JOURNAL*, **73**, 409 (1951).

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Preparation of Tetramethylammonium Monohydroxyfluoborate

BY CHARLES M. WHEELER, JR., RAYMOND D. BEAULIEU AND HAROLD W. BURNS

RECEIVED JUNE 29, 1954

The reaction of tetramethylammonium halides with methoxyfluoboric acid was studied in an attempt to prepare quaternary ammonium methoxyfluoborates. O'Leary and Wenske¹ have reported the compound mercury (II) oxide with methoxyfluoboric acid. These authors further stated that methoxyfluoborate compounds with cations more

(1) L. A. O'Leary and H. H. Wenske, *THIS JOURNAL*, **55**, 2117 (1933).

electropositive than mercury(II) could not be prepared due to immediate decomposition into the normal fluoborate. However, no specific compounds and no experimental data were reported to substantiate this observation. Meerwein and Pannwitz² have reported the preparation of sodium and potassium methoxyfluoborate by an indirect method, in which the respective methylates were treated with boron trifluoride dimethyl etherate.

The addition of solid tetramethylammonium chloride, bromide or iodide to methoxyfluoboric acid, at room temperature, resulted in immediate liberation of the appropriate hydrogen halide. The reaction mixture yielded a white solid when the solution was concentrated by evaporation or upon addition of small amounts of diethyl ether. Analysis showed the compound to be tetramethylammonium hydroxyfluoborate, melting point 414°.

Anal. Calcd. for (CH₃)₄NBF₃OH: C, 30.19; H, 8.34; B, 6.80; F, 35.85. Found³: C, 29.65, 29.93; H, 7.99, 7.80; B, 7.30, 6.90; F, 35.36, 35.65.

A separate series of experiments were performed to prepare tetramethylammonium hydroxyfluoborate from different starting materials. Monohydroxyfluoboric acid was titrated with a 10% aqueous solution of tetramethylammonium hydroxide to the phenolphthalein end-point. After neutralization a white solid was again precipitated by diethyl ether. The melting point and carbon, hydrogen and fluorine analyses for this solid agreed with similar data obtained for the solid reaction product from tetramethylammonium halides with methoxyfluoboric acid.

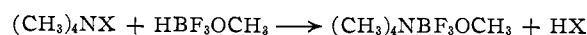
Although the analytical data confirmed the formation of tetramethylammonium monohydroxyfluoborate, an additional characterization was made with X-ray diffraction powder data. Identical powder patterns were obtained for the solid reaction products of tetramethylammonium halides with methoxyfluoboric acid and tetramethylammonium hydroxide with monohydroxyfluoboric acid. Table I lists these data for tetramethylammonium monohydroxyfluoborate.

TABLE I

X-RAY POWDER DATA FOR TETRAMETHYLAMMONIUM MONOHYDROXYFLUOBORATE, "d" FOLLOWED IN PARENTHESES BY RELATIVE INTENSITY

5.82 (6), 4.83 (10), 4.08 (100), 3.13 (20), 2.90 (1), 2.76 (10), 2.61 (1), 2.48 (40), 2.29 (20), 2.21 (6), 1.93 (20), 1.85 (1), 1.64 (18), 1.55 (3), 1.36 (1).

Nieuwland's⁴ proposed ionization for methoxyfluoboric acid indicates that a metathetical reaction of the acid with quaternary ammonium halides might be expected to proceed according to the equation



Greenwood⁵ has reported conductivity and viscosity data which conclusively demonstrated that

(2) H. Meerwein and W. Pannwitz, *J. prakt. Chem.*, **141**, 123 (1934).

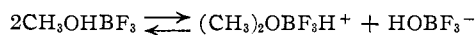
(3) Analyses were performed by Laboratory of Microchemistry, Dr. Carl Tiedcke, Teaneck, N. J.

(4) T. H. Vaughn, H. Bowlus and J. A. Nieuwland, *Proc. Indiana Acad. Sci.*, **40**, 203 (1931).

(5) N. N. Greenwood and R. L. Martin, *J. Chem. Soc.*, 751 (1953).

methoxyfluoboric acid ionizes to form methoxyfluoborate ions and protons solvated by one molecule of undissociated acid. However, Greenwood⁶ has cautioned that ionic dissociation schemes postulated for pure liquids do not necessarily represent the behavior of complexes in reaction media.

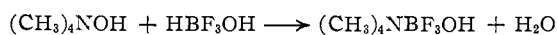
The formation of hydroxyfluoborates in the present research suggests the possibility of ionization during chemical reaction as



In support of this proposed equation, exploratory experiments have shown that the dimethyl ether boron trifluoride complex does solvate the proton. Results of these investigations will be reported at a later date.

(6) N. N. Greenwood and R. L. Martin. *Quart. Rev.*, (London), **8**, 1 (1954).

Metatheses of tetramethylammonium hydroxide with monohydroxyfluoboric acid is described by



Experimental

Methoxyfluoboric acid and hydroxyfluoboric acid were prepared by saturating anhydrous methanol and water with boron trifluoride, after which the compounds were purified by fractional recrystallization.^{5,7}

The X-ray powder diffraction photographs were made with copper radiation, filtered by nickel, using a Philips 57.3 mm. powder camera. The samples were mounted on Pyrex fibers. Intensities were estimated visually by comparison with a film of known intensity.

(7) J. C. McGrath, G. G. Stack and P. A. McCusker, *THIS JOURNAL*, **66**, 1263 (1944).

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[CONTRIBUTION FROM THE DEPARTMENT OF PLANT NUTRITION, UNIVERSITY OF CALIFORNIA, BERKELEY]

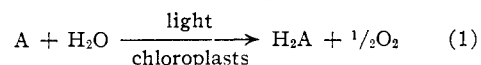
Photosynthesis by Isolated Chloroplasts. II. Photosynthetic Phosphorylation, the Conversion of Light into Phosphate Bond Energy

BY DANIEL I. ARNON, F. R. WHATLEY AND M. B. ALLEN*

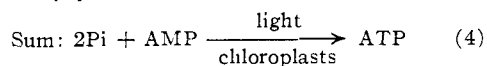
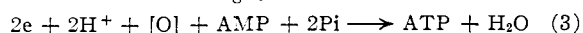
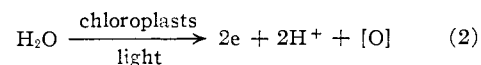
RECEIVED JUNE 4, 1954

Whole chloroplasts removed from green cells were found able to convert light into the chemical energy of pyrophosphate bonds of adenosine triphosphate (ATP). This photochemical esterification of inorganic phosphate outside the living cell, termed photosynthetic phosphorylation, is independent of CO₂ fixation and of the dark reactions of respiration. Photosynthetic phosphorylation has been demonstrated in a system consisting of washed spinach chloroplasts, NaCl, ascorbic acid and P³²-labeled orthophosphate, in the presence of a phosphate acceptor system (adenylic acid or hexokinase and glucose). ATP was identified as the product of the reaction (a) directly, by adsorption on norite followed by hydrolysis of labile phosphate and (b) indirectly, using hexokinase and glucose as an ATP acceptor system either during the progress of photosynthetic phosphorylation or following the termination of the reaction and the chemical isolation of ATP. In both cases the product of the hexokinase reaction, glucose-6-phosphate, was chromatographically identified.

Chloroplasts removed from living cells retain for an appreciable period of time that part of the photosynthetic apparatus which is responsible for the evolution of oxygen under the influence of light (Hill reaction)¹ in accordance with equation 1



in which A represents an electron or hydrogen acceptor other than carbon dioxide. Evidence has now been obtained that isolated whole chloroplasts, unaided by other cellular particles or enzyme systems, are also able to convert light energy into chemical energy in the form of the high energy pyrophosphate bonds of adenosine triphosphate (ATP). The following equations² represent a tentative scheme of the course of the reaction, in accordance with experimental facts now known.



* This investigation was supported in part by a research grant RG-2034 of the National Institutes of Health, Public Health Service. We wish to thank Dr. Hardin B. Jones for gifts of radioactive phosphorus.

(1) Hill, R., *Symp. Soc. Exp. Biol.* **5**, 222 (1951).

(2) This formulation is not intended to exclude the possibility that ATP is formed by the addition of pyrophosphate to AMP.

AMP and Pi represent adenosine-5-phosphate and orthophosphate. Adenosine diphosphate (ADP) was found to be as effective as AMP. This photochemical esterification of inorganic phosphate by chloroplasts, henceforth referred to as photosynthetic phosphorylation, provides a mechanism for converting light energy into ATP, independent of energy released by reoxidation of partly or wholly reduced products of photosynthetic CO₂ fixation.³

Photosynthetic phosphorylation was found to proceed unimpaired when the partial pressure of CO₂ was maintained at an extremely low level. The nature of the electron acceptor(s) in reaction 2, of the intermediate electron carriers involved, and the number of high-energy phosphate bonds generated in reaction 3 are being investigated. As shown in equation 4, photosynthetic phosphorylation is not accompanied by the evolution of oxygen. The brackets around the oxygen atom in reactions 2 and 3 are intended to denote that it has not yet been determined whether: (a) oxygen is released in reaction 2 and immediately consumed in reaction 3, thus giving no manometrically measurable pressure change, or (b) the oxygen in reaction 2 represents the formation of some oxidized substance within the chloroplast which is reduced in accordance with reaction 3. In this connection the recent observation by Lundegårdh⁴ of the oxidation of cyto-

(3) J. Franck, *Arch. Biochem. Biophys.*, **45**, 190 (1953).

(4) H. Lundegårdh, *Physiologia Plantarum*, **7**, 375 (1954)