

[CONTRIBUTION FROM THE RESEARCH LABORATORY, OLIN MATHIESON CHEMICAL CORPORATION]

Diborane from the Sodium Borohydride-Sulfuric Acid Reaction

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Diborane can be prepared in good yields from the reaction of sodium borohydride and sulfuric acid. The sulfur dioxide which is formed as a by-product of the reaction can be eliminated by use of methanesulfonic acid in place of sulfuric acid.

The mechanism of the hydrolysis of lithium borohydride by aqueous acid solutions was postulated by Kilpatrick and McKinney² to be a two-step process. The first step in the reaction is the formation of diborane, which immediately reacts with water to give hydrogen and boric acid. Subsequent work with sodium borohydride indicated a similar mechanism³ for its hydrolysis.

To check this mechanism the reaction of an alkali metal borohydride with anhydrous acid was examined. Good yields of diborane are obtained when solid sodium borohydride is added to sulfuric acid. The diborane prepared in this manner contains a small amount of impurity as sulfur dioxide which is separated easily from the diborane by conventional high vacuum fractionation techniques. Diborane, free of all impurities, can be prepared by substituting methanesulfonic acid for sulfuric acid in the reaction with sodium borohydride.

Experimental

A. Reagents. Sodium Borohydride.—Sodium borohydride obtained from Metal Hydrides, Inc., was used without further purification in most of the experiments reported here. The lump borohydride was ground in air and transferred to the reactor as quickly as possible. The analyses of the sodium borohydride by hydrolysis and titration⁴ indicated a purity of 95% NaBH₄. Sodium borohydride of 97% purity was obtained by recrystallization from water and then drying at 50° *in vacuo*.

Sulfuric Acid.—Baker and Adamson reagent-grade sulfuric acid was used without further purification. Stock acid was analyzed to be 96.4% H₂SO₄. The stock acid was diluted with distilled water to give solutions of 95.6, 92.9 and 78.8% H₂SO₄. The sulfuric acid containing 100% H₂SO₄ was prepared by the "fair and foggy" method⁵ which is the addition of fuming sulfuric acid (Baker and Adamson reagent-grade containing 15% SO₃) to the stock acid.

Methanesulfonic Acid.—Eastman practical-grade methanesulfonic acid was used without further treatment.

Sulfur Dioxide.—Sulfur dioxide, obtained from Mathieson Company, Inc., was purified by passing the gas through sulfuric acid (to remove any sulfur trioxide) and then through phosphorus pentoxide (to remove water).

B. Procedure.—The reactions were conducted in a three-necked round-bottomed flask, equipped with a magnetic stirring device and a solids addition assembly which was so placed in the center joint that the solid borohydride would fall directly into the acid solution without hitting the walls of the flask. Another joint was fitted with a stop-cock for use in introducing various gaseous atmospheres (nitrogen, hydrogen, helium or sulfur dioxide) and for sweeping the system during reaction. The third joint of the flask

was connected to a series of four U-tubes used for purifying and trapping the product. The first U-tube (following the reactor) was immersed in a Dry Ice (−78°) bath in order to remove traces of sulfuric acid which were entrained in the diborane stream. The other three U-tubes were cooled with liquid nitrogen (−196°) to collect all condensable products of the reaction. Following the U-tubes was a Toepler pump for pumping non-condensable gases into a calibrated gas buret.

For the generation of diborane *in vacuo* the following procedure was used. A large measured excess of sulfuric acid was added to the reaction flask and a weighed quantity of powdered sodium borohydride placed in the addition apparatus. The Dry Ice bath then was placed in position and the system was evacuated. After evacuation the liquid nitrogen baths were placed in position and the Toepler pump was started. The sodium borohydride was added slowly to the acid while the mixture was stirred magnetically. The pressure of the system was kept below 5 cm. during the addition. After the entire quantity of borohydride had been added, the sides of the flask were washed down with acid by means of the stirring bar and a hand magnet. The hydrogen evolved during the reaction was measured in a gas buret. The condensable gases then were separated and purified by fractional condensation through a −150° trap, and the volume of each fraction was measured. Identification was made by vapor pressure measurement and by mass spectrometer analysis (Consolidated Engineering Corporation, Model 21-103 Mass Spectrometer). The borohydride addition apparatus then was removed and flushed with dilute acid; these washings were titrated for boron. The sulfuric acid solution also was titrated for boron to obtain a complete boron balance. Usually B₂H₆ and SO₂ were the only products found; however, in an experiment in which the borohydride was added rapidly a trace quantity of H₂S also was observed. A decrease in yield of diborane was obtained when the reaction was run by reverse addition, *i.e.*, addition of sulfuric acid to sodium borohydride.

In those experiments in which the diborane was generated at atmospheric pressures, a slight modification of the above procedure was used. After the sulfuric acid was placed in the reaction flask and the sodium borohydride was placed in the addition assembly, all air was removed from the system by alternately evacuating and flushing the system with a dry gas (nitrogen, hydrogen, helium or sulfur dioxide). Care was taken in the first evacuation to prevent powdered NaBH₄ from contacting the acid while the air was still present in the system. The sodium borohydride then was added to the acid with the gas sweeping through the reactor and with Dry Ice and liquid nitrogen traps in position (except in the experiments involving sulfur dioxide gas, where a static system was used). After the addition of the borohydride, the system was evacuated and the condensed gases were fractionated and measured.

Results and Discussion

A number of sulfuric acid-sodium borohydride experiments, in which the concentrations of sulfuric acid were varied, were carried out under vacuum conditions. As the acid concentration was decreased from 96.4 to 78.8% H₂SO₄, the yield of diborane decreased from about 80 to 50% and the sulfur dioxide impurity was reduced from 20 to 1%. The decrease in yield is accounted for by hydrolysis of diborane. This was substantiated by hydrogen measurements which gave 95 to 100% accountability of diborane when calculated on the

(1) Aircraft Division, Hughes Tool Co., Culver City, California.

(2) M. Kilpatrick and C. D. McKinney, Jr., *THIS JOURNAL*, **72**, 5474 (1950).

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

(4) Analysis of sodium borohydride by hydrolysis with an excess of dilute acid is based upon the volume of hydrogen liberated; hence, this volume is a measure of the hydride ion content of the sample. The excess acid then is neutralized and the boron present titrated with standard alkali by the conventional mannitol method. The separate analyses for boron and hydride based on NaBH₄ content agreed within 1%.

(5) J. E. Kunzler, *Anal. Chem.*, **25**, 93 (1953).

basis of hydrolysis of lost diborane.⁶ Practically no loss of diborane was noted when a sample of gas was bubbled through concentrated and 100% sulfuric acids. Surprisingly, there was no appreciable increase in yield of diborane when the 100% sulfuric acid was used in the acid-borohydride reaction. The decrease in the amount of sulfur dioxide with decreasing concentration of acid may be due merely to increased solubility of the SO₂.

The experiment in which methanesulfonic acid replaced sulfuric acid was characterized by the complete absence of sulfur dioxide. The lower yield (76% B₂H₆) may have been due to the presence of moisture in the highly hygroscopic acid; however, only 91% of the diborane could be accounted for from hydrogen measurements calculated on the basis of hydrolysis of missing diborane.

(6) H. G. Weiss and I. Shapiro, *THIS JOURNAL*, **75**, 1221 (1953).

When the reactions were carried out at one atmosphere pressure (nitrogen, hydrogen or helium atmospheres), the sodium borohydride burned as it was added to the sulfuric acid solution. This flaming caused a deposit of sulfur in the reactor, gave lowered yields of diborane and a product contaminated with hydrogen sulfide. A series of experiments, in which rate of addition of borohydride was varied, showed that the flaming increased with increased rate of addition. When a sulfur dioxide atmosphere was used, more intense flaming occurred. That diborane itself was not necessarily involved was shown by the fact that sodium hydride also gave flaming under these conditions. It was possible to avoid flaming, and thus to prepare diborane in good yields at atmospheric pressure, by cooling the acid and stirring vigorously while adding the sodium borohydride very slowly.

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Mechanism of Oxidation of Hydrazine by Ferric Ethylenediaminetetraacetate (FeY⁻)^{1,2}

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The stoichiometry and kinetics of the reaction between ferric ethylenediaminetetraacetate (FeY⁻) and hydrazine in borax and phosphate buffers in the absence and presence of phenanthroline have been investigated. The oxidation product is mainly nitrogen; very small amounts of ammonia are formed, consistent with the reaction ratio, which is between 3.7 and 4.0 moles of FeY⁻ consumed per mole of hydrazine consumed. From the kinetic results it is established that the first step is reaction 1 of FeY⁻ and free base (not N₂H₅⁺), FeY⁻ + N₂H₄ → FeY⁻ + N₂H₃ + H⁺ (1). This reaction is reversible, and the N₂H₃ may reoxidize FeY⁻, FeY⁻ + N₂H₃ + H⁺ → FeY⁻ + N₂H₄ (-1) or be oxidized by FeY⁻, FeY⁻ + N₂H₃ → FeY⁻ + N₂H₂ + H⁺ (2). The latter reaction leads eventually to the formation of nitrogen after two further oxidations of N₂H₂. Also, the N₂H₃ may dimerize, leading eventually to the formation of ammonia and nitrogen. By the addition of sufficient phenanthroline to form rapidly the stable complex with iron(II), the reaction (-1) may be practically eliminated, and the over-all reaction becomes first order both to FeY⁻ and hydrazine. The rate constant is thus found to be $k_1 = 11$ liter mole⁻¹ min.⁻¹ at 40° and the activation energy 20 kcal. mole. When no phenanthroline is present, the occurrence of the back reaction leads to a rate which is approximately second order in FeY⁻, first order in hydrazine, and inversely first order in FeY⁻. The ratio of the rate constants k_{-1}/k_2 is found to be approximately 140 at pH 9 and 42 at pH 6.7, at 40°. The occurrence of the back reaction also is confirmed qualitatively by the pronounced acceleration of reaction rate caused by the EDTA complex of copper(II).

Introduction

This investigation originated in the discovery that the combination ferric ethylenediaminetetraacetate-hydrazine-organic hydroperoxide could be used for the initiation of emulsion polymerization of butadiene or styrene in alkaline medium at temperatures around 0°.³ In this paper the complexes of Fe(III) and Fe(II) with ethylenediaminetetraacetate (EDTA) are denoted as FeY⁻ and FeY⁻, respectively. Qualitatively it appeared that hydrazine reduced FeY⁻ to FeY⁻, and that the latter substance was oxidized by hydroperoxide to re-form FeY⁻ and a free radical derived from the hydroperoxide. In order to arrive at an understanding of the kinetics and mechanism of this recipe, it was necessary to investigate the kinetics and mechanism of the reaction between FeY⁻ and hydrazine in the absence and presence of hydroperoxide. Results

(1) This investigation was carried out under a grant from the National Science Foundation.

(2) From the M.S. thesis of H. Minato, July 1958. For brevity many pertinent data given in the thesis are omitted from this paper.

(3) I. M. Kolthoff and E. J. Meehan, *J. Polymer Sci.*, **9**, 343 (1952)

in the absence of hydroperoxide are presented in this paper.

Preliminary work on oxidation of hydrazine by FeY⁻ in borax and phosphate buffers was carried out in this Laboratory by Dr. C. Auerbach and Dr. P. K. Kapur in 1951-1952.⁴ In general their results tended to support the view that the primary step was a bimolecular reaction leading to formation of N₂H₃. However, the unexpected result was found that the reaction, which was initially relatively rapid, came to a virtual standstill before completion. This was thought to be due to a back reaction between FeY⁻ and the hydrazyl radical. If so, the addition of phenanthroline, which forms a much more stable complex with iron(II) than does EDTA, would be expected to prevent or minimize the back reaction. It was found in fact that the addition of phenanthroline prevented the pronounced decrease in rate, so that the reaction proceeded to completion and was approximately first order in ferric Versenate. However, the order with respect to hydrazine

(4) Reports to Office of Rubber Reserve.