

The method developed here furnishes values of ρ and V_e by an analytical solution of two simultaneous equations. Such solutions, of course, should also be obtainable by graphical methods^{7,9} without the necessity of introducing large experimental errors in the data. The effective volume in many cases cited,^{7,9} calculated according to the procedure developed here, is less than $M\bar{v}/N$. Since, in the previous treatment,^{7,9} $M\bar{v}/N$ has been interpreted as a part of the effective volume (*i.e.*, using the assumption that $V_e = M\bar{v}(1 + w/\bar{v}\rho)/N$), negative w values are, therefore, required to obtain consistency between intrinsic viscosity and frictional coefficient measurements in that procedure.

This shows clearly that the interpretation of w and the procedure used formerly^{7,9,10} are incorrect.

Accurate measurements of sedimentation constants, intrinsic viscosities, molecular weights, partial specific volumes and rotary diffusion constants for monodispersed native and denatured proteins in various solvents are required to explore the implications of the point of view presented here.

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ITHACA, NEW YORK

[CONTRIBUTION FROM THE NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

The Preparation of Anhydrous Perchloric Acid

BY G. FREDERICK SMITH

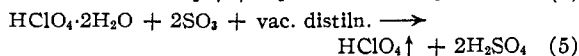
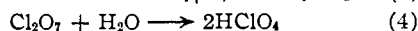
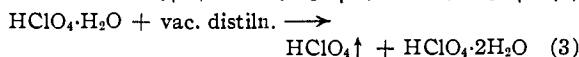
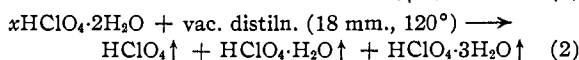
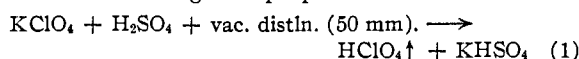
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An improved method is described for the preparation of anhydrous perchloric acid. The procedure involves the use of 72% perchloric acid and 20% fuming sulfuric acid. Mixtures of these acids in the proportions of 1 to 4, in the order given, serve as the reaction medium. The anhydrous perchloric acid is evolved from this mixture at pressures of 1 mm. or less and at temperatures from 27–75° in 75% yield. The product is completely recovered by chilling to Dry Ice temperatures. A discussion of the hazards involved is given. The process is favored also for the preparation of oxonium perchlorate OH_2ClO_4 . The finished product is not contaminated by sulfuric acid.

Introduction

For many operations in the study of perchloric acid and its salts the use of anhydrous perchloric acid may be required. Because of the hazards involved, a procedure for the preparation of this product, to be suitable, should involve the use of starting materials which are readily available in pure form, an apparatus assembly of simple but effective design, and a procedure that involves the least hazardous manipulations. The objective in the present investigation was the study of operative procedures leading to this goal.

Applicable Reactions.—The most appropriate reactions serving as a preparative scheme are



Reaction 1 has been employed frequently in studies involving the preparation of anhydrous perchloric acid for example by Roscoe¹ in one of the pioneer studies in this field. It is not a convenient process and was originally employed for the preparation of anhydrous perchloric acid to be at once diluted with water to 20 or 60% acid composition. This method was employed by van Wyk² and by van Emster³ in important early studies of the physical constants of anhydrous perchloric acid.

Reaction 2 was employed by Goehler and Smith⁴ in their study of the improved preparation of anhydrous perchloric acid and in the study of the dissociation of the concentrated acid at moderately low, (8–18 mm.), pressures. The yield of anhydrous acid by this procedure attained up to 10% of the starting material only.

Reaction 3 is convenient and effective but a supply of the monohydrated perchloric acid is dependent upon the preparation of anhydrous acid followed by dilution with water or the dihydrate of perchloric acid.

Reaction 4 involves the synthesis of the anhydride of perchloric acid, (Cl_2O_7), by the method of Michael and Cohn.⁵ Aqueous perchloric acid is dehydrated by reaction with excess phosphoric anhydride, (P_2O_5), followed by distillation.

Reaction 5 is utilized in the present study. The reaction ingredients taken are commercially available in pure form. The apparatus employed is of simple design. The reaction temperature covers the range 25–80°. The yield ranges from 50–80% and the raw materials may be recovered.

General Description of the Process.—Fuming sulfuric acid (15–20%), is added in various proportions to 72% perchloric acid. The heat of reaction is moderate and the reaction mixture is chilled to 25°. This mixture is digested at gradually increasing temperatures, 25–80°, and at low pressure to volatilize anhydrous perchloric acid. The finished product is condensed using Dry Ice as coolant and collected as a colorless liquid, freezing point -112° . Anhydrous perchloric acid may be stored without explosive decomposition for 30–60 days at liquid air temperatures and without the accumulation of the least coloration from decomposition products. Pure samples do not explode when stored at ordinary temperatures for approximately 30 days.

(1) H. E. Roscoe, *J. Chem. Soc.*, **16**, 82 (1863).

(2) H. S. van Wyk, *Z. anorg. Chem.*, **48**, 1 (1906).

(3) K. van Emster, *ibid.*, **52**, 270 (1907).

(4) O. E. Goehler and G. F. Smith, *Ind. Eng. Chem., Anal. Ed.*, **3**, 55 (1931).

(5) A. Michael and W. T. Cohn, *Am. Chem. J.*, **23**, 444 (1900).

It must be kept in mind, however, that even though this process is entirely without hazard, careless handling of the anhydrous perchloric acid may result in the most violent explosions. It must not be allowed to come in contact with dry wood, paper, rubber, cork, cotton, etc. Anhydrous HClO_4 in storage which becomes colored amber or darker must be immediately diluted with water for disposal and elimination of the hazard.

Apparatus.—The distillation assembly is shown in Fig. 1. The digestion flask is of 2000-ml. capacity. A standard taper ground joint, 28/15, serves to introduce the sample of mixed fuming sulfuric acid and perchloric acid and as a thermometer well. The digestion flask is provided with a large U-shaped delivery tube, 20 mm. outside diameter, terminating in a ball and socket (28/15) joint and a 10-mm. ring sealed extension tube which passes into the receiver flask. The condenser is of 50-mm. tubing 250 mm. long with a 20-mm. side arm leading to the exhaust pump and provided with a ball and socket ground joint (18/9) connection to the fume eradicator tube employed to protect the vacuum pump.

The fume eradicator tube is of 50-mm. tubing 375 mm. long terminating in a ball and socket joint (28/15) with an adaptor and stopcock serving to admit air by reverse flow at the end of the operation and to provide a connection to the vacuum gage. The fume eradicator tube is plugged at each end by glass wool with an alkali (KOH or NaOH) absorbant supported on a suitable carrier. Coarse grained Ascariite, or Caroxite or Mikohbite, may be employed.

All glass joints other than the exit end of the eradicator tube are lubricated using a drop of 72% perchloric acid. Regular grease lubrication may be used on the joints following the fume eradicator tube. A length of heavy wall rubber pressure tube is employed to serve for connections to the vacuum pump and vacuum gage.

The apparatus receiving reservoir is immersed in finely ground Dry Ice during the complete process. The Dry Ice is contained in a large silvered dewar flask. One charge of Dry Ice serves for several distillation operations.

A suitable Glas-col heating mantle with Variac voltage control serves to gradually heat the reaction flask. The finished product collects in the receiver as a clear, colorless, limpid liquid, which does not freeze at Dry Ice temperature. The use of liquid air as coolant would solidify the anhydrous perchloric acid and for this reason is not employed. The whole operation of the volatilization process should be conducted at less than 1 mm. pressure.

Preparational Procedure.—A 100- to 120-ml. sample of 72% perchloric acid is placed in the reaction flask which is immersed in an ice-bath for cooling. Oleum (20% fuming sulfuric acid), in the ratio of 3, 4 or 5 volumes to one volume of perchloric acid is gradually added. If the reverse process is employed and the perchloric acid is added to the oleum the mixtures become yellow due to the formation of Cl_2O_7 , which, while not hazardous, is undesirable. The reaction flask is now mounted with the receiver and fume eradicator in place and Dry Ice provided for cooling the receiver flask. The reaction is started by reducing the pressure to not more than 1 mm. (and preferably less) and with the reaction mixture at 20–25°. A steady stream of the anhydrous acid is volatilized from the flask into the receiver even at the lower temperature of the starting reaction. The reaction mixture accumulates bubbles of gaseous HClO_4 which break at the surface of the reaction mixture as though it were a boiling phenomenon.

The temperature is gradually raised to 30° per hour allowing about 2 hours to complete each batch of material. At the higher temperatures, 65–86°, no ebullition results and the last available anhydrous perchloric acid passes into the receiver without ebullition. At the end of the reaction the pressure is adjusted to that of the outside air and the receiver, after the removal of the Dry Ice coolant, is allowed to attain laboratory temperature. From the original weight of the receiver the weight of the anhydrous HClO_4 is determined. To prove that the product is in fact anhydrous the calculated weight of 72% perchloric acid is added and the reaction mixture is cooled to 50° whereupon it should solidify. This procedure is recommended if the anhydrous acid is not to be used within a reasonable time of storage.

A test of the finished product for sulfuric acid was made and it was found to be entirely absent because all the free SO_2 of the starting oleum has been converted to H_2SO_4 and the temperature of the reaction is not sufficient to volatilize

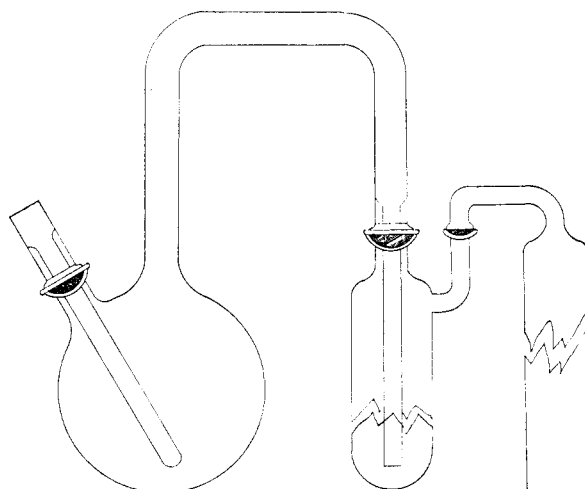


Fig. 1.

sulfuric acid into the condensed anhydrous perchloric acid being prepared. The test was made upon the reaction mixture of 5 volumes of 20% oleum to 1 volume of 72% perchloric acid and on the fraction obtained over the temperature range 65 to 85°.

A record of a set of experimental runs is given in Table I.

TABLE I

THE PREPARATION OF ANHYDROUS PERCHLORIC ACID FROM VARYING PROPORTIONS BY VOLUME OF 20% OLEUM AND 72% PERCHLORIC ACID

	Reaction mixture, ml.		Temp. of reaction, °C.	Yield anhydrous HClO_4 , g.	Yield, %
	72% HClO_4	20% Oleum			
1	100	300	29 to 72	75	62
2	120	480	22.5 to 77	108	75
3	100	500	29 to 65	62	51
	100	500	65 to 86	19	
					77 total

Table I shows that the most convenient combination of reactants is 1 volume of 72% perchloric acid and 4 volumes of 20% oleum. The anhydrous acid prepared from 120 ml. of 72% perchloric acid with a 75% yield is sufficient to prepare approximately 9 ounces (254 g.) of oxonium perchlorate, OH_2ClO_4 , m.p. 49.90°. Experiment 3 was done in two stages to better serve as a test portion for the detection of the presence or absence of sulfuric acid as contaminant.

The residue in the distilling flask may be heated *in vacuo* to such temperature that the last trace of perchloric acid has been volatilized, at temperatures above 85–86°, after the first pure anhydrous perchloric acid has been volatilized and the receiving flask has been changed. By this procedure the remainder of the perchloric acid is recovered slightly contaminated with sulfuric acid and the residue of concentrated sulfuric acid from the operation employed for other purposes. The accumulated sulfuric acid impure distillate may then be used to make more starting material by the addition of oleum. By this scheme all the starting materials are completely recovered.

Conclusions.—The above described experimental work was carried out without a protective shield being employed for any of the experimentation. This attests to the safety of the operations. It is to be recommended, however, that in the habitual application of these experiments a shield of some sort be employed between the operator and the apparatus to make assurance doubly sure. It is a matter of certainty that anhydrous perchloric acid is not nearly as hazardous to make and handle as the general opinion of the product would indicate. The crystalline monohydrate may be stored in-

definitely at ordinary temperatures. Samples have been stored in sealed capsules for years without discoloration or decomposition.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

New Developments in the Chemistry of Diborane and the Borohydrides. I. General Summary¹

BY H. I. SCHLESINGER AND HERBERT C. BROWN² IN COLLABORATION WITH B. ABRAHAM, A. C. BOND, NORMAN DAVIDSON, A. E. FINHOLT, JAMES R. GILBREATH, HENRY HOEKSTRA, LEO HORVITZ, EARL K. HYDE, J. J. KATZ, J. KNIGHT, R. A. LAD, DARWIN L. MAYFIELD, LOUIS RAPP, D. M. RITTER, ANTHONY M. SCHWARTZ, IRVING SHEFT, L. D. TUCK AND A. O. WALKER

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The present is the first of a series of papers describing new developments in the methods of preparation and in the chemistry of diborane and of the borohydrides. New and practical methods for the preparation of borohydrides (a) from diborane, and (b) without the use of diborane are discussed. As a result of the availability of borohydrides, prepared without the use of diborane, methods, far more satisfactory than those hitherto known for the preparation of the latter, have been developed. The investigation has led to the preparation of the hitherto unknown borohydrides of sodium, of potassium and of uranium, and some of their derivatives, as well as of a new type of substance, such as sodium trimethoxyborohydride, $\text{NaBH}(\text{OCH}_3)_3$, formed by the addition of compounds of trivalent boron to alkali metal hydrides. Sodium borohydride, as well as sodium trimethoxyborohydride, are of special interest because of their potential usefulness as reducing agents and sources for the generation of hydrogen; uranium(IV) borohydride and its derivatives are of interest because they are the most volatile compounds of uranium except the hexafluoride. The present paper surveys numerous new observations made and organizes the subject matter in the light of the principle which largely guided the research, namely, the application of the Lewis generalized acid-base concept to the reactions of diborane, of the salt-like hydrides and of the borohydrides. Detailed description of the new preparative methods and data confirming the reaction equations herein presented as well as supporting the composition of the new substances are deferred to the remaining papers of the series.

Introduction

Early in 1941 we were asked to undertake the synthesis of new volatile compounds of uranium. We began our search with a study of uranium(IV) and -(VI) complexes derived from 1,3-diketones and related chelating agents. As will be described in a later paper, it soon became evident, from a study of the changes produced in the vapor tensions of the complexes by altering the structure of the diketone, that a vapor tension of 0.1 mm. at a temperature of 130° could probably not be exceeded.

The fact that the borohydrides of aluminum and of beryllium had proved to be the most volatile compounds of these elements³ suggested that we attempt to prepare a borohydride of uranium. For this purpose, procedures different from those employed previously for the preparation of borohydrides had to be developed, since the earlier methods consisted of the reaction of diborane with a metal alkyl,^{3,4} and no alkyls of uranium were known. The desired result was achieved by the interaction of uranium(IV) fluoride with aluminum borohydride.

The resulting uranium(IV) borohydride, $\text{U}(\text{BH}_4)_4$, as well as the methyl derivatives, $\text{U}(\text{BH}_4)_3(\text{BH}_3\text{CH}_3)$ and $\text{U}(\text{BH}_3\text{CH}_3)_4$, actually proved to be the most volatile uranium compounds other than

the hexafluoride.⁵ Equally interesting are the developments which resulted from our efforts to improve the methods of preparing the starting materials and the intermediates required for the preparation of the uranium borohydrides. As a result of these efforts many new types of reactions were observed and at least partially investigated, hitherto unknown compounds were discovered, and the field of the chemistry of the hydrogen compounds of boron was greatly enlarged.

The urgency of the investigation made it impossible to pursue each new reaction and to characterize each new substance with the utmost thoroughness. Enough data have, however, been obtained to establish beyond reasonable doubt the over-all course of the new reactions and the compositions of the new substances described herein. We, therefore, considered it desirable and appropriate, in spite of certain lacunae, to record our observations in order to make them available to other workers.

Because of the large amount of material to be covered, we have prefaced the papers which describe the experimental and other details of the numerous compounds and reactions involved, by this introductory one, which is essentially a survey, without experimental details, of the papers which are to follow. Furthermore, to coordinate the subject matter, we have organized the presentation according to a central principle which had proved to be an extremely useful guide in the investigation. This theme is the application of the Lewis generalized acid-base concept⁶ to the reactions of diborane and of compounds related to it. Although

(1) Most of the work reported herein constitutes a part of investigations carried out under contracts with the National Defense Research Committee, with the Office of Scientific Research and Development and with the Signal Corps, Ground Signal Agency during the years 1940-1944. They were continued under Navy auspices during 1944-1946. Most of the results were originally described in the final reports on contracts NDC-rc-56, OEM.sr-117 and 368 and N173 s-9058, 9820 and 10,421.

(2) Department of Chemistry, Purdue University.

(3) (a) H. I. Schlesinger, R. T. Sanderson and A. B. Burg, *THIS JOURNAL*, **62**, 3421 (1940); (b) A. B. Burg and H. I. Schlesinger, *ibid.*, **62**, 3425 (1940).

(4) H. I. Schlesinger and H. C. Brown, *ibid.*, **62**, 3429 (1940).

(5) Papers X and XI of this series: (a) H. I. Schlesinger and H. C. Brown, *ibid.*, **75**, 219 (1953); (b) H. I. Schlesinger, H. C. Brown, L. Horvitz, A. C. Bond, L. D. Tuck and A. O. Walker, *ibid.*, **75**, 222 (1953).

(6) G. N. Lewis, *J. Franklin Inst.*, **226**, 293 (1938).