bilities. When the hydroxy acetal (II) was treated with ethyl formate or ethyl orthoformate under conditions identical to those used for the preparation of 3,3-diethoxy-2,2-dimethylpropyl formate (III), a very complex mixture of products was formed but no ester could be isolated.

We, therefore, believe that the ester is formed not by a secondary process from the hydroxy acetal but as a result of the direct interaction of ethyl orthoformate with the hydroxy aldehyde. The scope and implications of the reaction are being investigated.

Experimental[3]

Reaction of Hydroxypivaldehyde with Ethyl Orthoformate.—A mixture of 51.0 g. (0.5 mole) of hydroxypivaldehyde,[4] 75.0 g. (0.52 mole) of ethyl orthoformate, 75 ml. of dry ethanol and 1.0 g. of dry ammonium chloride was boiled under reflux for thirty minutes. The volatile products were removed by distilling the reaction mixture until the temperature of the vapors reached 80°. The residual material was washed with two 50-ml. portions of distilled water and the washings were extracted twice with 50-ml. portions of ether. The water washed product and the ether extracts were then combined and dried over anhydrous magnesium sulfate. After evaporation of the ether, the product was distilled through an eight-inch electrically-heated column packed with glass helices. Distillation yielded 31.0 g. (32%) of 3,3-diethoxy-2,2-dimethylpropyl formate, b. p. 93–94° (13 mm.), $n^{20}D$ 1.4200, d^{20}_{20} 0.9633. An infrared absorption spectrum indicated the presence of a carbonyl group, ether linkages, and the absence of a hydroxyl group.[5]

Anal.[6] Calcd. for $C_{10}H_{20}O_4$: C, 58.80; H, 9.94; MR 53.60; mol. wt., 204. Found: C, 58.90; H, 10.05; MR, 53.33; mol. wt., 203.

Preparation of Hydroxypivaldehyde Diethyl Acetal.—To a solution prepared from 7.0 g. (0.1 mole) of potassium hydroxide in 75 ml. of dry ethanol was added 20.0 g. (0.1 mole) of 3,3-diethoxy-2,2-dimethylpropyl formate. The mixture became warm, turned light yellow, and a flocculent white solid precipitated. Distilled water (1.5 ml.) was added and the mixture was boiled under reflux for three hours. After removing as much alcohol as possible on the steam-bath, the mixture was cooled, and 100 ml. of ether was added. Potassium formate precipitated and was removed by suction filtration. After drying on a clay plate the salt melted at 162–165°. A mixed melting point with an authentic sample melted at 164–165°.[7] After removing the ether from the filtrate, distillation yielded 14.5 g. (84%) of hydroxypivaldehyde diethylacetal, b. p. 55° (1.0 mm.), $n^{20}D$ 1.4259, d^{20}_{20} 0.9335.

Anal. Calcd. for $C_9H_{20}O_3$: C, 61.33; H, 11.44; MR, 48.58. Found: C, 61.43; H, 11.48; MR, 48.36.

Reaction of Hydroxypivaldehyde Diethyl Acetal with Ethyl Orthoformate.—Hydroxypivaldehyde diethylacetal (10.0 g., 0.057 mole) was treated with ethyl orthoformate under conditions identical with those described for the reaction of hydroxypivaldehyde with ethyl orthoformate. After drying and removing the ether it was attempted to distill the reaction mixture as before. A small amount of ethyl orthoformate and some material boiling at 85–185° (1.0 mm.) was obtained but the major part of the reaction mixture remained in the distilling flask. No pure components could be separated from the volatile portion on redistillation. The high boiling point of this material showed that no hydroxypivaldehyde diethylacetal nor 3,3-diethoxy-2,2-dimethylpropyl formate could have been present.

Reaction of Hydroxypivaldehyde Diethyl Acetal with Ethyl Formate.—Freshly prepared hydroxypivaldehyde diethyl acetal (10.0 g., 0.057 mole) was treated with ethyl formate (4.2 g., 0.057 mole) under conditions identical with those described for the reaction of hydroxypivaldehyde with ethyl orthoformate. After removal of the ether, 4.4 g. of ethyl formate (b. p. 52–54°) was recovered which must have contained a small amount of alcohol. On attempted distillation only a clear tough resin was obtained.

Summary

When ethyl orthoformate is allowed to react with hydroxypivaldehyde the only product which can be isolated is 3,3-diethoxy-2,2-dimethylpropyl formate. This product arises from the direct interaction of the hydroxyaldehyde with ethyl orthoformate and not as a secondary reaction product of hydroxypivaldehyde diethylacetal.

(3) All melting and boiling points are uncorrected.

(4) Stiller, Harris, Finkelstein, Keresztesy and Folkers, THIS JOURNAL, **62**, 1787 (1942).

(5) We are indebted to Dr. Foil A. Miller and Mrs. J. L. Johnson for the determination and the interpretation of the spectrum of this sample.

(6) We are indebted to Miss Theta Spoor for the carbon–hydrogen microanalyses reported in this paper.

(7) The melting point of pure potassium formate is 165–167°.

URBANA, ILLINOIS RECEIVED AUGUST 26, 1948

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE CORN PRODUCTS REFINING COMPANY]

Osmotic Pressure Studies on Corn Amylose

BY F. C. CLEVELAND AND R. W. KERR

The average molecular magnitude of the two fractions of starch still is a matter of some uncertainty. Even for the amylose fraction of corn starch, which has probably received more attention than any other starch component, estimations of size have been made which vary by 100%, or more. On the basis of sedimentation and diffusion studies, Fox[1] set a minimum value of 540 glucose units by the use of the acetate of a subfraction of corn amylose in methyl acetate solutions. Dumbrow[2] used a similar product and obtained a value of 375 by similar methods. Foster and Hixon[3] calculated that the DP_n for corn amylose was 260 from osmotic pressure measurements of the acetate in chloroform. Principally from viscosity measurements by Foster and Hixon,[4] Foster[5] has estimated that corn amylose, extracted

(1) T. J. Fox, Dissertation, Columbia University, New York, N. Y., 1943.

(2) B. A. Dumbrow, Dissertation, Columbia University, New York, N. Y., 1944.

(3) J. Foster and R. Hixon, THIS JOURNAL, **66**, 557 (1944).

(4) J. Foster and R. Hixon, *ibid.*, **65**, 618 (1943).

(5) J. E. Foster, Dissertation, Iowa State College, Ames, Iowa, 1943.

from the starch by water at 75°, has a chain length of 175 glucose units. Foster and Hixon used the starch fraction dissolved in ethylenediamine. Meyer, Bernfeld and Hohenemser[6] obtained a value of 270 by osmotic pressure measurements in tetrachloroethane of the acetate of amylose prepared by extensively extracting corn starch with hot water. Caesar, Gruenhut and Cushing[7] have recently reported a value of 220 for corn amylose, using the nitrate in ethyl acetate according to the isopiestic method of Barger.

Precise work in fundamental starch chemistry necessitates having a more accurate knowledge of the size of starch components than is currently available. Work based on improperly prepared fractions and their derivatives and on methods which lack a rigorous derivation may be eliminated from consideration. Even so, the remaining work leads to ambiguous conclusions. A series of osmotic pressure measurements made on the same sample of a carefully prepared corn amylose acetate in three solvents, chloroform, 2,4-pentanedione and pyridine, are reported below. These results are given to point out the magnitude of the problem and to establish perhaps a basis for the interpretation and correlation of available data on other physical measurements which have been reported.

Experimental

Preparation of Corn A-Fraction (Corn Amylose).—Defatted corn starch was treated according to the method of Schoch[8] by using Pentasol to precipitate the amylose from an autoclaved sol. The product was recovered by means of a super-centrifuge, redissolved in hot water and recrystallized by the addition of butanol. The yield was 20.8% by weight. The amount of iodine absorbed by the product was measured potentiometrically by Schoch's[9] modification of the method originated by Bates, French and Rundle.[10] This value was found to be 19.2% and indicates exceptionally high purity.

Preparation of the Acetyl Derivative.—Acetylation was performed according to a modification of the method of Mullen and Pacsu.[11] The starch fraction was dispersed in hot aqueous pyridine, the water removed by distillation of the pyridine–water azeotrope and then acetic anhydride was added which accomplished the major part of the acetylation. The modification consisted of adding fused sodium acetate at this point and refluxing for two periods each of one hour on separate days. After recovery of the product by pouring the reaction solution into a large volume of water, the material was disintegrated by wet grinding for a few seconds in a Waring Blendor. The acetate was recovered by filtration and washed five times with 100 times its weight of water, each washing involving a forty-eight-hour soaking period in the wash water. The yield was 97% and the acetyl content, measured by the method of Murray, Staud and Gray,[12] was 44.8%.

(6) K. H. Meyer, P. Bernfeld and W. Hohenemser, *Helv. Chim. Acta*, **23**, 885 (1940).

(7) G. V. Caesar, N. S. Gruenhut and M. L. Cushing, THIS JOURNAL, **69**, 671 (1947).

(8) T. J. Schoch, THIS JOURNAL, **64**, 2957 (1942).

(9) T. J. Schoch, in Radley's "Starch and Its Derivatives," 3rd edition, in press.

(10) F. L. Bates, D. French and R. E. Rundle, THIS JOURNAL, **65**, 142 (1943).

(11) J. W. Mullen and E. Pacsu, *Ind. Eng. Chem.*, **34**, 1209 (1942).

(12) T. F. Murray, C. J. Staud and H. LeB. Gray, *Ind. Eng. Chem., Anal. Ed.*, **3**, 269 (1931).

Osmotic Pressure Measurements.—Osmotic pressure measurements were made in a cell substantially as described by Fuoss and Mead.[13] The cell was placed in a wooden box and completely surrounded by cotton waste except for the protruding capillary tubes, filling tubes and valves. A thermometer was fastened directly to the metal cell. The assembly was then placed within a glass windowed cabinet provided with heating and cooling coils, air circulation and a mercury thermoregulator. The temperature of the cell was maintained at 30.00 ± 0.05°. Liquid levels in the capillaries were measured by use of a Gaertner Model M-908 cathetometer with an accuracy of ±0.05 mm. The dynamic method for determining osmotic pressures described by Fuoss and Mead[13] was used. These results were in good agreement with frequent determinations by the static method when chloroform and pentanedione were used as solvents. In the case of pyridine, movement of solvent was so slow that measurements based on early dynamic readings created an appreciable error and static measurements were employed entirely. In several determinations with pyridine the results of the static tests at twenty-four hours were checked again at seventy-two hours. No further increase in pressure was observed after the first twenty-four hours.

Uncoated, du Pont No. 450 cellophane, pretreated as described below, was used for membranes. Treatment consisted of soaking the membrane for from six to twenty-four hours in a series of solvent mixtures

Water (50°)
50% water–50% ethyl alcohol
95% ethyl alcohol
50% ethyl alcohol–50% amyl alcohol
100% amyl alcohol
75% amyl alcohol–25% solvent
50% amyl alcohol–50% solvent
25% amyl alcohol–75% solvent
100% solvent

All solvents used were purified by usual procedures starting with reagent grade liquids. Chloroform was distilled over calcium chloride and gave a neutral reaction. 2,4-Pentanedione was purified according to the method of Denoon.[14] As prepared, its reaction was neutral, but the liquid gave a slight acid reaction when exposed to air. Pyridine was refluxed and distilled over barium oxide.

The treated membranes were tested for permeability to the amylose acetates by evaporation of the liquid in the solvent side of the osmometer. In no case was a non-volatile residue obtained.

In preparing solutions, a standard procedure was adopted unless otherwise noted. The acetate was wet with part of the solvent and allowed to stand in a flask overnight. The next morning the flask was heated for fifteen minutes at 55°. For pyridine a temperature of 95° was used. The flask was cooled to 30° and the solution made up to volume.

In setting up the cell, solutions of least concentration were used first with new membranes. After use, the cell was drained, rinsed with solvent and then washed three times with the next higher concentration. A new membrane was used at the beginning of each series. In no case was the membrane found to be permeable to the amylose acetate samples. Some adsorption of the amylose acetate on the cellophane membrane was noted. This was particularly true in very dilute solutions (of the order of 0.05 to 0.20 g. per 100 ml.) and very low osmotic pressures were obtained. Accordingly, measurements were made at concentrations of 0.35 g. per 100 ml. and higher and then only after several prolonged soakings and washings with solutions of the concentration under study.

The osmotic pressures observed were expressed as cm. head of water, divided by the concentration in grams per 100 ml. and these values were plotted against concentration. The curve was extrapolated to zero concentration

(13) R. M. Fuoss and D. J. Mead, *J. Phys. Chem.*, **47**, 59 (1943).

(14) C. E. Denoon, Jr., in Allen's "Organic Syntheses," Vol. 20, New York, N. Y., 1940, p. 6.

and the value $[\pi/C]_{c=0}$ determined. Molecular weights were calculated as DP_n values from the equation

$$DP_n = \frac{RT}{[\pi/C]_{c=0} \times M} = \frac{2.57 \times 10^5}{[\pi/C]_{c=0} \times 288}$$

wherein

R is the gas constant at 30°
T is the absolute temperature
M is the molar weight of an anhydro glucose triacetate group
π is the osmotic pressure expressed as cm. head of water

Discussion of Results

The results of osmotic pressure measurements on corn amylose acetate in solutions of chloroform, pentanedione and pyridine are shown in Fig. 1, and calculated; apparent DP_n values are 455, 675 and 1370, respectively (Table I). All of the liquids employed are good solvents for the acetate, using "good" in the ordinary sense, when comparison is made with other solvents which have been used and reported for amylose and other carbohydrate esters, such solvents for example as methyl acetate, ethyl acetate, tetrachloroethane and benzene. The rate of solution was reasonably high, particularly in the case of chloroform and pentanedione. The solutions were sparkling clear and remained so after standing at room temperatures for several days. In the case of pyridine the observation was made, however, that on prolonged standing, *e.g.*, thirty days or more, solutions containing 1% of corn amylose acetate began to precipitate a gel-like material on the bottom of the flask.

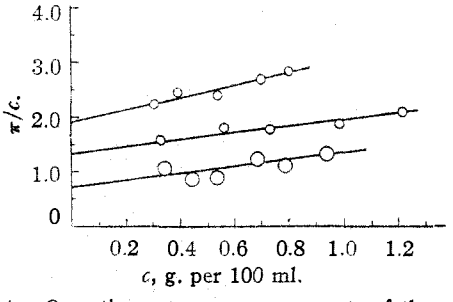

Fig. 1.—Osmotic pressure measurements of the acetate of corn amylose (no. 27) in: chloroform (top curve), 2,4-pentanedione (middle curve), pyridine (bottom curve).

It is well known that the amyloses are polydisperse.[15,16,17] Accordingly, one may expect some variation between samples when substantially the same procedure is used for isolation owing to minor variations in technique and the possibility of a subfractionating effect during repeated recrystallizations of the product. Another sample of corn amylose (no. 45), gave a value of 495 when the acetate was used in chloroform. Corn amylose prepared by butanol precipitation and recrystallization from aqueous butanol (C 1/13), and previously used to prepare subfractions,[17] was converted into the acetate and from osmotic pressure measurements in chloroform a DP_n of 435 was calculated in this solvent.

(15) K. H. Meyer, P. Bernfeld and E. Wolff, *Helv. Chim. Acta*, **23**, 854 (1940).
(16) R. W. Kerr, *Arch. Biochem.*, **7**, 377 (1945).
(17) R. W. Kerr, THIS JOURNAL, **67**, 2268 (1945).

TABLE I

APPARENT DP_n VALUES FOR CORN AMYLOSE ACETATE SAMPLES IN VARIOUS SOLVENTS AT 30°

Sample	DP_n in chloroform	DP_n in pentanedione	DP_n in pyridine
Corn amylose (no. 27)[a]	455	675	1370
Corn amylose (no. 45)[a]	495	...	
Corn amylose (no. C 1/13)[b]	435	...	
Corn amylose subfraction I	250	370	
Corn amylose subfraction II	390	575	
Corn amylose subfraction III	525	795	
Corn amylose subfraction IV	675	...	
Corn crystalline amylose	225	465	

[a] Pentasol precipitated. [b] Butanol precipitated.

Four subfractions of the amylose sample, C 1/13, were prepared by ethylenediamine–ethyl ether phase separation technique.[17] These subfractions were acetylated and osmotic pressure measurements made in chloroform and in pentanedione solutions at 30°. The results for calculated DP_n values are shown in Table I. Considerable variation, over 100%, was found in the chain lengths of the amylose subfractions. Again, higher values, about 50% higher, were found when pentanedione was used than when chloroform was employed as the solvent.

A corn amylose fraction, called corn crystalline amylose,[16] prepared by extracting corn starch with water at 75° and crystallizing the product from the extract by the addition of butanol, formed an acetate which had an apparent DP_n of 225 in chloroform and 465 in pentanedione. This product is of the same type studied by Dumbrow[2] in methyl acetate solution. Foster[5] estimated a DP of 175 for this fraction from viscosity measurements in ethylenediamine, as stated above.

The great variation in length of the amylose chains comprising any one sample no doubt explains in part the different values obtained when different systems are used for the measurement of average DP values. It would be expected that osmotic pressure measurements from which number average molecular weights are calculated would give different results for corn amylose than viscosity or light-scattering data which are functions of weight-average molecular weight. Normally expected variations between samples would account for some discrepancy among the results of several investigators using the same system of measurement. However, these considerations do not account for the very large differences between the results, above reported, and presented in Table I when the same samples were used in the same apparatus and the solvent employed was the only variable. These data suggest that amylose derivatives are associated in organic solvents, to different extents, depending on the solvent.

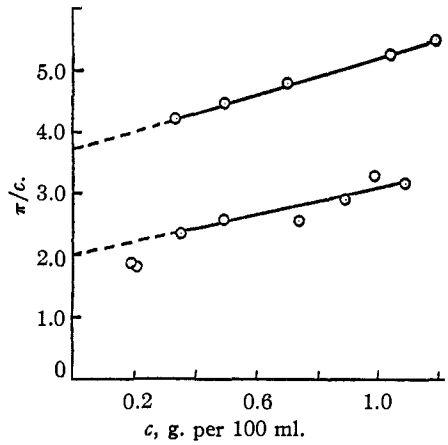

Fig. 2.—Osmotic pressure measurements, acetate of corn crystalline amylose in: chloroform (top curve), 2,4-pentanedione (bottom curve).

Doty, Wagner and Singer[18] have called attention to the fact that polymers may not be completely dissociated in solution and that the simple, difficultly refutable assumption that we are dealing with molecular dispersions in physical measurements on high polymer solutions is not always justified. This work deals principally with polyvinyl chloride polymers or co-polymers with the acetate, and the conclusions are limited by the consideration that linear organic halogen compounds might be expected to associate because of electronegative halogens. One would also expect the carbohydrates which have many hydroxyl groups along their chains to associate, for which reason they are usually derivatized for physical studies. However, carbohydrate esters, such as cellulose acetate, were shown by Doty and his coworkers also to give different osmotically determined molecular weights in acetone and in methyl "cellosolve." Cellulose acetate fraction 9 of Sookne and Harris[19] was found to have a molecular weight of 53,000 in acetone and 74,400 in methyl "cellosolve."

We had available a portion of this fraction 9 and found that its number average molecular weight in chloroform[20] at 30° was 47,600. This result invites drawing the general conclusion that linear carbohydrate acetates are associated to different degrees in various solvents and that association is least in chloroform.

Steurer[21] and others have proposed from the great difference in osmotic pressure of ethyl cellulose in the two solvents, chloroform and benzene, that the lower osmotic pressure curve for benzene solutions, relating π/C to C, turns abruptly upward as infinite dilution is approached and at zero concentration π/C equals the value for that of chloroform solutions. Possibly this is so. However, it should be noted that at concentrations of 0.1 g. per 100 ml. and less, the experimental error and inherent errors become very large and data taken in this concentration range are less reliable. Accordingly, we have made few observations at very low concentrations, but of those that were taken in pentanedione, the majority of values fell below rather than above the curve extrapolated from more reproducible values.[22] We have attributed these lower osmotic pressure values at low concentration to the effect of adsorption of solute by the new membrane. On the other hand, if one reuses cellophane membranes for very dilute solutions which have previously been employed at solute concentrations in the range of 0.3 to 1.2 g. per 100 ml., then one obtains, with amylose acetate at least, abnormally high osmotic pressures.

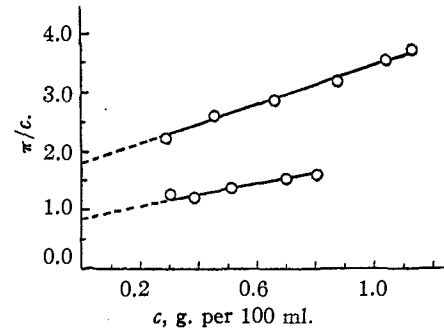

Fig. 3.—Osmotic pressure measurements in chloroform of the acetates of: corn amylose, no. 45 (top curve); tapioca amylose (bottom curve).

Even were curves obtained in some solvents which showed a radical change in slope from positive to negative within the concentration range below 0.1 gram per 100 ml., one could hardly expect to extrapolate these curves with any degree of certainty and the conclusion would still follow that the improper choice of solvent may lead to an inaccurate estimate of molecular weight. Furthermore, such data would not be inconsistent with the view that the solute associated more in these solvents than in those which gave a straight line relationship at some higher osmotic pressure level.

The association noted for corn amylose acetate in pentanedione and pyridine appears to be exaggerated for starch molecules, both linear and branched, which have a *DP* greater than that of the corn amylose samples. For example, Foster and Hixon[3] and F. Horan[23] observed that the amylose fraction from potato starch formed an acetate which swelled and only partially dissolved, even in chloroform. Tapioca amylose acetate (Pentasol precipitable fraction) appears to be very nearly the limit in respect to molecular size for visual solubility in chloroform, or rather lack of visual insolubility. The acetate swells at first and then appears finally to give a homogeneous dis-

(18) P. Doty, H. Wagner and S. Singer, *J. Phys. Colloid Chem.*, **51**, 32 (1947).

(19) A. Sookne and M. Harris, *Ind. Eng. Chem.*, **37**, 475 (1945).

(20) Contained by weight 2% added ethanol.

(21) E. Steurer, *Z. physik. Chem.*, **A190**, 1 (1941).

(22) Note, for example, lower curve, Fig. 2.

(23) F. Horan, Dissertation, Columbia University, New York, N. Y., 1944.

persion which is optically void on heating to 55°. The apparent DP_n in chloroform was found to be 1050 at 30°. The effect was even more pronounced in the case of corn amylopectin acetate (fraction not precipitated by Pentasol). During acetylation of this fraction, the reaction mixture set to a gel when the ratio of carbohydrate to pyridine plus acetic anhydride was 2 to 100 and it was necessary to reduce this ratio to 1 to 100 in order to obtain a fluid medium and to complete the acetylation. The triacetate remained insoluble, for the most part, even with prolonged boiling in chloroform or mixtures of chloroform and alcohol. However, it was found that corn amylopectin subfraction III[16] forms a triacetate which dissolves in chloroform and for which a DP_n value of 635 was found. The acetates of subfractions of higher molecular weight were only partially soluble. These experiments leave no doubt of the very great association which can exist between these carbohydrate molecules (or molecular entanglement), particularly in very high molecular weight ranges and which may operate to some extent even in the low molecular weight ranges.

The reluctance of carbohydrate derivatives to disperse molecularly in organic solvents leaves open to question the results of all physical measurements of molecular weight which involve a study of solutions whether the method consists of osmotic pressure, viscosity, light scattering or sedimentation measurements. It is believed that the extent of dissociation depends not only on the solvent which is employed but possibly also on the temperatures used and on the type of starch derivative, and that these considerations explain in part at least the wide spread in values reported in the past for the chain length of corn amylose.

For the present in fundamental studies it would seem wise to adopt the use of a readily prepared derivative, such as the acetate, and a solvent such as chloroform which gives a low order of molecular weight values by osmotic pressure measurements and a definite procedure in respect to temperature and time, until these values can be checked by a completely independent method. Boiling temperatures are suggested for preparing the solutions and 30° for measurement.

Conclusions

The apparent DP_n values for the acetates of corn amylose and its subfractions have been calculated from osmotic pressure determinations using selected solvents. Of those used, chloroform gave the lowest DP_n values; the acetate of one corn amylose sample prepared by Pentasol precipitation was found to have a DP_n of 455 and another 495. The acetate of a butanol precipitated corn amylose had a DP_n of 435. Subfractions of the latter varied in DP_n between 250 and 675.

Higher values for DP_n were found in other solvents tried and this may be explained as being due to association of the acetates in these solvents. Starch acetate samples tend to become visibly insoluble, or partly insoluble in organic solvents as the DP exceeds that of corn amylose. Tapioca amylose acetate appeared to be very nearly the limit in respect to molecular size for solubility in chloroform and showed a DP_n of 1050 in this solvent.

ARGO, ILLINOIS RECEIVED JULY 16, 1948

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

The Preparation of Boron Hydrides by the Reduction of Boron Halides

BY DALLAS T. HURD

It recently (1945) has been found that boron hydrides, specifically diborane and diborane monohalides, can be synthesized by the reduction of boron halide vapor with hydrogen in the presence of metals[1] at elevated temperatures.

In addition it has been discovered that the hydrides of the alkali and alkaline earth metals will reduce gaseous boron halides to diborane at temperatures above about 200°.[2]

Experimental

A. Reductions Involving Metals.—1. Boron trichloride gas[3] and hydrogen in *ca.* 1:3 ratio were passed through a vertical bed of −20 mesh aluminum granules in a 1" Pyrex tube heated to 350°. After a short induction period aluminum chloride was observed subliming out of the reaction zone and the gas issuing from the reactor became spontaneously inflammable, burning with a green flame.

Chemical tests on samples of the exit gas indicated the presence of boron hydrides. These included the standard tests such as the decolorization of hanging drops of permanganate solution, formation of chocolate brown precipitate on paper soaked in silver nitrate solution, formation of hydrogen bubbles in hanging water droplets, as well as other chemical reactions characteristic of the boranes. The exit gas gave negative results on all of these tests until the temperature necessary for reaction had been reached.

To study the reaction in more detail a larger apparatus was designed (Fig. 1) comprising a reactor tube $2^1/_2$ in. in diameter, heated in a cylindrical furnace, followed by a trap to collect the aluminum chloride formed during the reaction and by traps at −80 and −190° to collect the reaction products. The side arm leading from the reactor to the aluminum chloride trap was kept warm electrically to avoid deposition of the halide in the tube. The boron chloride and hydrogen were metered in through rotameters, the hydrogen being purified in a conventional set-up. The

(1) A general criterion for the metal is that it be more electropositive than boron.

(2) Mention should be made of the reactions in ether solution between boron halides and the hydrides of electropositive metals to yield boron hydrides discovered by H. I. Schlesinger and his coworkers at Chicago, Ill.

(3) Boron trichloride supplied by the Cooper Metallurgical Laboratories, Cleveland, Ohio; purity over 98%.