precipitate which was mainly calcium sulfate. One-half gram of the sediment from the long-term degradation (calcium content 23.5%; carbon dioxide evoluted, 19.9%) was heated with 5 ml. of *N* sulfuric acid at 100° for 3 hours, neutralized with barium carbonate and filtered. The filtrate was treated with Amberlite resin IR-120(H). The resulting solution when examined by paper chromatography with solvents A and B and spray C, gave spots corresponding to erythronic acid and its lactone, glyoxylic acid and erythritol. The solution was stirred with 10 g. of Amberlite resin IR-400(OH) at room temperature for 20 hours, filtered and evaporated to dryness. The residue (10 mg.) crystallized slowly and gave an X-ray diffraction pattern identical with that of authentic erythritol.

**Identification of Major Acidic Products.**—The stock barium salt solution from the short-term sodium hydroxide degradation was stirred with an excess of Amberlite resin IR-120(H) at room temperature for 30 minutes. The solution was transferred uniformly to sheets of Whatman 3MM paper which had been washed with water and dried. Approximately 5 meq. of the acid fraction were applied to each 46 × 56 cm. paper without heating and the paper was irrigated with solvent A for 6 hours. Guide strips were sprayed with A and B and the relevant zones were eluted with water. The following components were identified:

DL-**2,4-Dihydroxybutyric acid** was identified as its anilide, m.p. 115–116° alone or in admixture with an authentic sample kindly supplied by Dr. J. W. Green, Institute of Paper Chemistry, Appleton, Wis. It was also characterized as its brucine salt,[16] m.p. 172–174°.

*Anal.* Calcd. for $C_{27}H_{36}O_8N_2$: N, 5.5. Found: N, 5.5.

**Glycolic acid** was identified as its amide, m.p. and mixed m.p. 119–120°, and also as its 4-bromophenacyl ester, m.p. and mixed m.p. 137–138°.

DL-**2,4-Dihydroxybutyrolactone** was identified as the anilide, m.p. and mixed m.p. 115–116°.

**Quantitative Determination of Degradation Products.**—Total acidity was determined by treating an aliquot portion of the barium salt stock solution with an appropriate amount of newly washed Amberlite resin IR-120(H). The filtrate was back titrated after treatment at room temperature for 30 minutes with a fourfold excess of 0.025 *N* sodium hydroxide.

Volatile acidity and formic acid were determined as described by Richards and Sephton.[17]

Quantitative determinations of the neutral fraction of the four alkali-degraded oxystarch samples were made by direct weighing of the dried solids after deionizing with ion exchange resins.

Five of the acidic degradation products were determined semi-quantitatively for non-volatile acids by paper chromatography. A portion of the barium salt stock solution was treated with an excess of Amberlite resin IR-120(H) at room temperature for 30 minutes and filtered. The exact acid concentration of the filtrate was obtained by back titration after addition of an excess of alkali. An aliquot portion of the acid sample containing 0.2–0.5 meq. of acid was applied to the center 12 cm. section of a piece of water-washed Whatman 3 MM paper (24 × 57 cm.) and an equal loading was applied to the outer 3-cm. guide strips. After developing the papers with solvent A for 6 hours, the guide strips were sprayed with sprays A and B and the relevant zones from the center section eluted with water (25 ml. per zone). The resinous acidic substance ($R_1$ 0–0.25) and the supposed Cannizzaro rearrangement products ($R_1$ 0.28–0.30) were dried and weighed directly after combining the eluates from several such papers. Separation of these two components was incomplete due to extensive streaking on the chromatograms. The yields recorded are therefore very approximate.

For glycolic acid and DL-2,4-dihydroxybutyric acid and its lactone, the concentrations of the acids in the respective eluates were determined spectrophotometrically. Calkins' method[18] was found to be applicable to both acids after separation. Glycolic acid gave a pink color with an absorption maximum at 5400 Å. while DL-2,4-dihydroxybutyric acid gave a greenish-yellow color which showed an absorption maximum at 4550 Å. Similar amounts of authentic samples of glycolic acid when subjected to the same process gave a recovery of 67 ± 5%. In the absence of a sufficient supply of authentic DL-2,4-dihydroxybutyric acid for a similar calibration, the same correction factor was applied to both acids. The results of all of the above determinations are summarized in Table I. The recovery of acid from this type of determination is, however, dependent on the loading of the paper and the acid yields are approximate and possibly subject to error of the order of ±10%.

**Acknowledgment.**—The authors wish to express their thanks to the American Maize Products Co. for partial support of this work.

(16) J. U. Nef, *Ann.*, **376**, 1 (1910).

(17) G. N. Richards and H. H. Sephton, *J. Chem. Soc.*, 4492 (1957).

(18) V. P. Calkins, *Anal. Chem.*, **15**, 762 (1943).

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[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, PURDUE UNIVERSITY]

# Oxidation of Amylopectin with Hydrogen Peroxide at Different Hydrogen Ion Concentrations[1,2]

BY ROY L. WHISTLER AND RICHARD SCHWEIGER

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Amylopectin is rapidly attacked by hydrogen peroxide over the *p*H range 7 to 12.5. The initial effect is depolymerization which is followed by a rapid and extensive oxidation presumably of end units, to produce mainly carbon dioxide and formic acid in 1:6 ratio and lesser amounts of methylglyoxal, D-arabinose and D-erythronic, glyoxylic and glycolic acids. Recovery of large quantities of D-glucose from the hydrolyzed oxidation products obtained by use of large amounts of hydrogen peroxide tends to confirm the theory that the attack occurs principally on reducing end units and other oxidized sites.

Sodium or hydrogen peroxide often has been used for bleaching ground wood and semi-chemical pulp and, at times, has been used as a final stage in the bleaching of sulfite and sulfate pulps. In addition to its action on lignin and color bodies, peroxide reacts with cellulose,[3,4] although in commercial operations the effect may be minor because of the low oxidant levels used. While the initial effect of hydrogen peroxide on cellulose is depolymerization, Haskins and Hogsed[5] detected in the products from oxidized cotton linters, carbon di-

(1) Journal Paper No. 1363 of the Purdue University Agricultural Experiment Station.

(2) This is paper number 5 in a series concerning Action of Oxidants on Carbohydrates. Previous papers in the series are: R. L. Whistler and S. J. Kazeniac, *J. Org. Chem.*, **21**, 468 (1956); R. L. Whistler, E. G. Linke and S. J. Kazeniac, THIS JOURNAL, **78**, 4704 (1956); R. L. Whistler and R. Schweiger, *ibid.*, **79**, 6460 (1957); R. L. Whistler and R. Schweiger, *ibid.*, **80**, 5701 (1958).

(3) H. Staudinger and J. Jurisch, *Papier-Fabr., Tech. Tl.*, **35**, 459 (1937).

(4) J. Jurisch, *Jentgen's Kunstseide u. Zellwolle*, **23**, 266 (1941).

(5) J. F. Haskins and M. J. Hogsed, *J. Org. Chem.*, **15**, 1264 (1950).

oxide, formic, oxalic, lactic and D-arabonic acids as well as other unidentified aldonic acids and lactones. Russian workers[6,7] find that hydrogen peroxide causes rapid depolymerization of cellulose with production of small amounts of ketonic, aldehydic and acidic products and also find that the reaction is catalyzed by ferrous ions. Similar results have been observed when hydrogen peroxide has been allowed to react with starch; and numerous reports occur in the older literature.[8]

More precise information concerning the reaction of hydrogen peroxide on cellulose and starch will come to light as additional reaction products are isolated and characterized. In this paper information is reported on the products obtained from hydrogen peroxide oxidation of corn starch amylopectin at different *p*H levels. Amylopectin is selected since it readily dissolves and, hence, probably gives a more homogeneous reaction than would whole starch or amylose. Oxidations are performed at *p*H levels of 3, 5, 7, 9, 11 and 12.5 at 25° in the dark without added catalyst. When hydrogen peroxide at the rate of two moles per mole of D-glucose unit is added to a 1.25% aqueous dispersion of amylopectin, loss of hydrogen peroxide depends upon solution *p*H as illustrated in Fig. 1. Consumption of hydrogen peroxide is

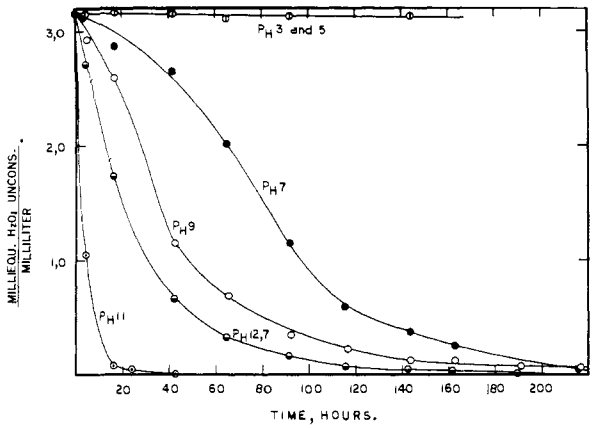


Fig. 1.—Hydrogen peroxide consumption in corn starch amylopectin solutions at 25°.

greatest at *p*H 11 and is relatively slow at *p*H 7. At *p*H 3 and 5 no oxidant is consumed within a period of several days. Oxygen evolution from hydrogen peroxide decomposition occurs at all *p*H levels greater than 5 and is most intense at *p*H 11. Curves shown in Fig. 1 are not corrected for this decomposition.

Hydrogen peroxide, especially under alkaline conditions, brings about a rapid depolymerization of amylopectin as shown by following changes in viscosity. Such changes for 2% amylopectin solutions are shown in Fig. 2. The dotted line represents viscosity changes in the absence of hydrogen peroxide for a 2% amylopectin solution at

(6) V. I. Ivanov, E. D. Stakheeva-Kaverzneva and Z. I. Kuznetsova, *Izvest. Akad. Nauk S.S.S.R. Otdel., Kim. Nauk*, 374 (1953).

(7) V. I. Ivanov, E. D. Stakheeva-Kaverzneva and Z. I. Kuznetsova, *Doklady Akad. Nauk S.S.S.R.*, **86**, 301 (1952).

(8) See, for example, the review by R. W. Kerr, "Chemistry and Industry of Starch," Academic Press, Inc., New York, N. Y., 1950, p. 326.

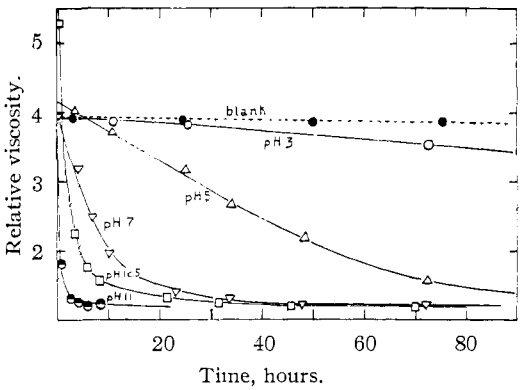


Fig. 2.—Rate of change in relative viscosity of 2.0% amylopectin solutions during oxidation with 2 mole equivalents of hydrogen peroxide per mole of D-glucose unit at 25°.

*p*H 9. At *p*H 11 the blank value began at a relative viscosity of 4.3 and ended at 3.6, and at *p*H 12.5 the relative viscosity began at 16.7 and decreased to 10.5 after 78 hr. While the curves representing changes in relative viscosity are similar in shape to the curves representing rate of hydrogen peroxide decrease (Fig. 1), they differ markedly on the time scale. Decrease in viscosity is very rapid and solutions approach the viscosity of water within a few hours.

Acidification of alkaline reaction mixtures released carbon dioxide indicating that some portions of the carbohydrate molecules are extensively oxidized. However, when such reaction mixtures are hydrolyzed in *N* sulfuric acid, the presence of large quantities of D-glucose is indicated by chromatograms. Thus many D-glucose units of the amylopectin are not attacked during the oxidation, but those that are attacked are extensively degraded.

To obtain sufficient reaction products for easy identification, a large quantity of amylopectin is oxidized at *p*H 11 using 18 moles of hydrogen peroxide per mole of D-glucose unit. When the reaction products from this oxidation are hydrolyzed and chromatographed, the same components are in evidence as are obtained from the small-scale oxidation shown in Fig. 1.

PRODUCTS ISOLATED AND IDENTIFIED FROM THE LARGE-SCALE OXIDATION

| Product | Moles/mole D-glucose unit in amylopectin |
|---|---|
| D-Glucose | 0.46 |
| Formic acid | 1.0 |
| Carbon dioxide | 0.15 |
| Methylglyoxal | .008 |
| D-Arabinose | .003 |
| D-Erythronic acid | ... |
| Glyoxylic acid | ... |
| Glycolic acid | ... |

When the reaction products are hydrolyzed and the mixture concentrated by distillation, formic acid and methylglyoxal volatilize and collect in the distillate. Formic acid is identified by its reaction with mercuric chloride and by its reduction to formaldehyde. The amount present is estimated

both by weighing the mercurous chloride formed and by titration. Methylglyoxal is identified and quantitatively determined as the 2,4-dinitrophenylosazone. D-Glucose is isolated by direct crystallization from the concentrated hydrolyzate. Chromatography of the concentrate on a cellulose column also permits the separation of D-arabinose, identified as the phenylosazone. Ether extraction of the concentrate separates a mixture of erythronic, glyoxylic and glycolic acids. The first is identified as its lactone. Glyoxylic acid is identified as the 2,4-dinitrophenylhydrazone and glycolic acid is identified as its amide. While the yields of these acids are not easily measured, glycolic acid appears to be in greatest quantity, seemingly surpassing the amount of methylglyoxal.

Viscosity minimum in the oxidation mixture is reached after only a small portion of the oxidant is consumed. Oxidation starts slowly and then becomes more rapid as is especially evident in the curves for *p*H 7 and 9 of Fig. 1. These observations suggest that depolymerization makes available reactive sites which permit the initiation of an extensive oxidation. Such second stage reaction gives rise principally to carbon dioxide and formic acid. Other oxidation products which are found in small amounts do not seem to be intermediates in the formation of carbon dioxide or of formic acid, for if they were, the ratio of carbon dioxide to formic acid would be higher. In particular, the carboxylated compounds should, on further oxidation, yield carbon dioxide from a large proportion of their total carbon. Thus, these compounds seem to be products of side reactions. D-Erythronic and glyoxylic acids may be formed from oxidative cleavage between carbon atoms C2 and C3 and methylglyoxal may derive from glyceraldehyde or dihydroxyacetone,[9,10] which in turn results from cleavage between carbon atoms C3 and C4. D-Arabinose may result from oxidative chain shortening of D-gluconic acid. Since no dibasic acids are found, carbon atom C6 seems to undergo little independent oxidation.

The ratio of carbon dioxide to formic acid (1:6) is much smaller than that found by others[11] who have treated simple sugars with hydrogen peroxide.

## Experimental

**Amylopectin.**—Commercial corn starch was fractionated by the pentasol method of Wilson, Schoch and Hudson.[12] Amylopectin was obtained from the concentrated centrifugate by precipitation into ethanol and was dried by four successive passages through fresh absolute ethanol. During each filtration care was taken to draw no air through the filter cake. Ethanol was removed from the final cake by placing it in a vacuum desiccator over calcium chloride. The product was a fine white powder.

**Amylopectin Oxidation.**—Amylopectin was dissolved in hot water and cooled to give a clear solution which, after addition of two moles of hydrogen peroxide per mole of D-glucose unit, contained 1.25% polysaccharide. Oxidations were performed at 25° in the dark at *p*H levels of 3, 5, 7, 9, 11 and 12.5. In those oxidations in which products were to be identified or quantitatively determined, the *p*H levels were adjusted with either sulfuric acid or sodium hydroxide solution and maintained at very near these values throughout the reaction by the addition, when necessary, of sodium hydroxide to neutralize acids formed. In oxidations in which the rate of hydrogen peroxide consumption was to be measured more accurately, the solution *p*H was controlled with sodium bicarbonate for *p*H 7, with a mixture of sodium bicarbonate and sodium carbonate for *p*H 9, with sodium carbonate for *p*H 11 and with sodium hydroxide for *p*H 12.5.

Hydrogen peroxide content of solutions was measured by allowing it to oxidize iodide to iodine which was determined by titration with thiosulfate. Thus to 30 ml. of 0.2 *N* potassium iodide containing a small amount of ammonium molybdate was added 20 ml. of *N* sulfuric acid. To this mixture a 1-ml. aliquot of the oxidation mixture was slowly added and allowed to stand 10 min. Liberated iodine was then titrated with a standard sodium thiosulfate solution. No hydrogen peroxide was consumed in 3 days by the amylopectin solutions at *p*H 3 and 5. At other *p*H levels oxidation occurred as shown by the rate of hydrogen peroxide consumption in Fig. 1. The optical rotation decreased slightly in oxidations at each *p*H value except those at *p*H 3 and 5. Decrease in relative viscosity of 2.0% amylopectin solutions during oxidation with 2 mole equivalents of hydrogen peroxide at different *p*H levels is shown in Fig. 2. At *p*H 3 and 5 the relative viscosity decreased slowly, which may have been indicative of a slight depolymerization.

**Hydrolysis of Oxidized Amylopectin.**—After consumption of hydrogen peroxide at each *p*H level above 5 the solutions were made 1 *N* in sulfuric acid and refluxed 6 hr. and sulfate was removed as the barium salt. To prevent coprecipitation of organic matter most of the barium sulfate was filtered from the solution before neutralization was complete. The final small barium sulfate precipitate removed at the neutral point did not seem to be contaminated with organic matter. The filtrate was passed through a column of cation exchange resin,[13] Amberlite IR-120(H), and concentrated to a thin sirup. For paper chromatography ethyl acetate–acetic acid–formic acid–water (18:3:1:4 v./v.) was used as irrigant, and ammoniacal silver nitrate was used as spray reagent.[14] Eight components were observed with $R_g$ values of 3.84, 2.73, 2.35, 2.11, 1.43, 1.00, 0.33 and 0.13, respectively.

**Large-scale Preparation.**—Since chromatographic analysis suggested hydrogen peroxide oxidation products in relatively small quantity, a larger-scale preparation was undertaken at *p*H 11 where the reaction was more rapid and where greater quantities of products seemed to occur. Ten grams of amylopectin was oxidized as described above, but with 18 moles of hydrogen peroxide per mole of D-glucose unit added in 3 successive portions over a 4-day period. Subsequent portions of oxidant were added when the preceding ones were entirely consumed. Continuous adjustment was made to keep the *p*H close to 11. The oxidation mixture was hydrolyzed, freed of sulfate ion and concentrated as described above. On paper chromatography the same eight components were observed as previously described and no new ones were seen when chromatograms were made with several other irrigants or when different spray reagents were used.

**D-Glucose.**—The thin concentrate was seeded with D-glucose and the sugar allowed to crystallize at room temperature for about 6 hr. Then about 6 volumes of ethanol were added slowly with constant slow stirring. After standing overnight at about 5° crystalline D-glucose was filtered. It was chromatographically pure; yield 34 mole per cent. On recrystallization the m.p. was not altered by admixture with authentic D-glucose. Reaction with phenylhydrazine gave D-glucose phenylosazone, m.p. 211°, not depressed by admixture with authentic material.

**D-Arabinose.**—The ethanolic solution was concentrated to about 0.1 volume and the thin sirup extracted with ether in a liquid–liquid extractor for 3 days. The aqueous residue was chromatographed on a cellulose column 30 mm. × 570 mm. with ethyl acetate–pyridine–water (8:2:1 v./v.) as irrigant. The first component eluted was D-arabinose, which was identified as its phenylosazone, m.p. 159–161°, undepressed on admixture with authentic material; $R_g$ value in ethyl acetate–acetic acid–formic acid–water as described above was 1.43, identical with the value for an authentic

(9) C. Neuberg, E. Faerber, A. Levite and E. Schwenk, *Biochem. Z.*, **83**, 264 (1917).

(10) K. Bernhauer and B. Görlich, *ibid.*, **212**, 452 (1929).

(11) See, for example, THIS JOURNAL, **67**, 1654 (1945).

(12) E. J. Wilson, Jr., T. J. Schoch and C. S. Hudson, *ibid.*, **65**, 1380 (1943).

(13) Product of Rohm and Haas Co., Philadelphia, Pa.

(14) S. M. Partridge, *Nature*, **158**, 270 (1946).

sample of D-arabinose. An aliquot of column effluent was analyzed for D-arabinose content by the method of Willstätter and Schudel[15] to give a calculated total yield equivalent to 0.0025 mole of D-arabinose per mole of D-glucose unit of the amylopectin.

The second compound from the cellulose column was D-glucose, identified as its phenylosazone, m.p. 211°, and by its chromatographic flow rate. The amount of D-glucose in the column effluent was determined by Willstätter and Schudel titration as 11.7 mole per cent. of the amylopectin. Thus the combined D-glucose yields are equivalent to 50.9% or 0.457 mole per mole of D-glucose unit in the amylopectin.

**Incompletely Hydrolyzed Fragments.**—Since nothing further seemed to be removed from the cellulose column with the ethyl acetate–pyridine–water irrigant, the column was washed with ethanol. This removed two trace components with $R_g$ values of 0.33 and 0.14. This mixture, after hydrolysis with 2 *N* sulfuric acid solution at reflux for 5 hr. and after paper chromatographic analysis with the above irrigant, gave evidence of the presence of glucose, arabinose and erythronolactone. No trace of the original two unknown components remained on this chromatogram.

**D-Erythronolactone.**—The ether extract was evaporated to a sirup (0.66 g.) and placed on a cellulose column 30 mm. × 570 mm. The irrigant was ethyl acetate–acetic acid–formic acid–water (18:3:1:4 v./v.). Separation of components was not complete, but the center fraction of each effluent component was separated.

The first effluent component was D-erythronolactone, identified by crystallization as long prisms from ethyl acetate–amyl acetate (3:1 v./v.); m.p. 104°, not depressed when admixed with authentic material. The $R_g$ value was 2.73.

**Glyoxylic Acid.**—The second effluent component was glyoxylic acid, which was difficult to obtain free of erythronolactone. It also contained a trace of unknown component of $R_g$ 2.11. Glyoxylic acid was identified by treatment with 2,4-dinitrophenylhydrazine to obtain crystalline yellow needles of glyoxylic acid 2,4-dinitrophenylhydrazone, m.p. 186–188°, not depressed when admixed with authentic material.

**Glycolic Acid.**—Finally there emerged from the column a fraction which contained glycolic acid, identified as the amide. For this preparation the fraction was decolorized with charcoal, concentrated to a sirup, dissolved in methanol and treated with diazomethane in ether. The solvent was then evaporated and the sirup distilled at 4 mm. to give a colorless distillate which was dissolved in methanol saturated with ammonia. After standing overnight at 5° the solution was concentrated, whereupon crystals appeared. Recrystallization was made from hot ethyl acetate to yield glycolamide, m.p. 114–116°, undepressed by admixture with authentic material.

**Formic Acid.**—During concentration of the acid hydrolyzate directly from the oxidation the distillate was collected in an ice-cooled receiver. Titration of an aliquot of the distillate with standard base showed the presence of acid. If assumed to be formic acid, the amount corresponded to 0.96 equivalent per D-glucose unit of the amylopectin. A second determination of formic acid was obtained by reaction with mercuric chloride. For this an aliquot of the solution was mixed with mercuric chloride, the mixture acidified with hydrochloric acid and heated on a steam-bath for 1 hr. Precipitated mercurous chloride was filtered in a tared crucible, dried and weighed. The amount of formic acid present was thereby calculated as one mole per mole of D-glucose unit of the amylopectin.

Proof of the presence of formic acid was obtained by treatment of an aliquot of distillate with magnesium. After filtration the formaldehyde produced was allowed to react with 2,4-dinitrophenylhydrazine in dilute hydrochloric acid. A small amount of precipitate which formed in the hot solution was probably methylglyoxal 2,4-dinitrophenylosazone and was removed by filtration. On cooling the filtrate, yellow needles of formaldehyde 2,4-dinitrophenylhydrazone separated, m.p. 162–164°, undepressed when mixed with authentic material.

**Methylglyoxal.**—Another portion of the distillate was heated with 2,4-dinitrophenylhydrazine to produce an orange precipitate of methylglyoxal 2,4-dinitrophenylhydrazone, m.p. 288–289°; after recrystallization from nitrobenzene, m.p. 297–298°. Calcd.: N, 25.86. Found: N, 25.82. The yield of hydrazone indicated 0.008 mole of methylglyoxal per mole of D-glucose unit of the amylopectin. However, this titrimetric procedure appears to give high results with structures of the glyoxal type.

**Carbon Dioxide.**—Carbon dioxide produced during amylopectin oxidation with hydrogen peroxide was determined for the reaction at *p*H 11. Ten grams of amylopectin was dissolved in 650 ml. of hot water and oxidized with 18 moles of hydrogen peroxide per mole of glucose unit as described above. The solution was acidified with sulfuric acid and the mixture refluxed for 30 min. in a contained system swept by a slow stream of nitrogen. Carbon dioxide evolved was measured by passage into a 0.5 *N* solution of sodium hydroxide. Differential titration of the alkali with 0.1 *N* oxalic acid, after addition of barium chloride in excess of the carbonate present, gave a measure of the carbon dioxide absorbed. As a result 0.152 mole of carbon dioxide per mole of D-glucose unit was measured by this method.

**Viscosity Change.**—Twelve grams of amylopectin was dissolved in hot water by stirring for several hr. After division into 12 equal parts, half served as controls and half were oxidized. Each was brought to a volume of 25 ml. after adjustment in pairs to the proper *p*H value and addition of oxidant to one member of each pair. Adjustments to the proper *p*H values of 3, 5, 7, 9, 11 and 12.5 were made by addition of hydrochloric acid, sodium bicarbonate, sodium carbonate or sodium hydroxide. Hydrogen peroxide from a stock of 30% concentration was added to give 2 moles of oxidant per mole of D-glucose unit. All solutions contained amylopectin at 2% concentration. They were kept in the dark at 25° and the *p*H values were frequently checked and corrected if necessary. The changes in viscosity of the solutions were followed by frequent measurements with an Ostwald–Cannon–Fenske viscometer. Since the densities of the solutions were near 1.0, density was ignored in the formula for relative viscosity. Results are shown in Fig. 2.

Measurements with solutions containing 0.2 mole of oxidant per mole of D-glucose unit gave similar, but slower, decreases in viscosity.

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(15) R. Willstätter and G. Schudel, *Ber.*, **51**, 780 (1918).