of solution to be dissipated, and drawing straight lines through the remaining points, we find that a value of k determined from curve 2 is 2% low and a value of k determined from curve 1 is 15% low.

Since the magnitude of the error depends upon the velocity of the reaction, it seems not improbable that this might account for the trend which Brønsted and Wynne-Jones[3] observed as they varied the concentration of the hydrogen ion. Their assumption that the trend was due to oxidation of the acetal would require an amount of acid to be produced which seems quite unlikely.

In Table II we summarize the various determinations of the hydrogen ion catalyzed rate constant for the hydrolysis of acetal in water. If the experiments were not done at 25°, the rate at this temperature was calculated using the heat of activation as determined by Kilpatrick and his students.

Summary

We have analyzed the effects of the heat of solution and the heat of reaction on the determination of rate constants by the dilatometric method.

We have devised a magnetically stirred dilatometer which minimizes the errors due to these effects.

We have determined the heat of solution and the heat of hydrolysis of acetal in water, in 4 M sodium chloride and in 1 M potassium nitrate, and also the volume change due to hydrolysis in these systems.

We have also determined the hydrogen ion catalyzed rate constant for the reaction in these solvents at 25°.

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[CONTRIBUTION FROM THE IOWA AGRICULTURAL EXPERIMENT STATION]

The Configuration of Starch in the Starch–Iodine Complex. III. X-Ray Diffraction Studies of the Starch–Iodine Complex[1]

BY R. E. RUNDLE AND DEXTER FRENCH

Introduction

In two previous papers[2] optical evidence has been presented that under certain conditions starch chains possess a helical configuration. The modifications which have been examined and which appear to have this configuration are: (1) the "V"[3] modification of starch, *i. e.*, starch precipitated with certain alcohols, and (2) the starch–iodine complex, where the starch helices appear to contain the iodine molecules, as in Fig. 1 of (a).[2] On the other hand, in granular and retrograded starches the starch chains appear to be extended into some essentially linear configuration.[4] Earlier work on the helical configuration is reviewed briefly in the previous papers.[2]

Reported here is an investigation of the starch–iodine complex by X-ray diffraction. This work provides important confirmatory evidence for the structure previously proposed for the starch–iodine complex; moreover, it suggests certain additional features of the structure.

Preparation of the Starch–Iodine Complex.—Recently, Schoch's[5] fractionation of starch has made available the amylose component of starch.[6] In this component the regularities of the starch chains are not interrupted by frequent branching.[2,5,7] As a result, all the crystalline modifications of the amylose component are superior to those same crystalline modifications for whole starch.[8] All iodine complexes used in this investigation were prepared from amylose.

The starch–iodine complex or, more strictly, the amylose–iodine complex was prepared by

(1) Journal Paper No. J-1106 of the Iowa Agricultural Experiment Station, Ames, Iowa, Project No. 639. Supported in part by a grant from the Corn Industries Research Foundation.

(2) (a) R. Rundle and R. Baldwin, THIS JOURNAL, **65**, 554 (1943); (b) R. Rundle and D. French, *ibid.*, **65**, 558 (1943).

(3) Starch exists in several crystalline modifications. Classification can be made on the basis of X-ray diffraction patterns. For nomenclature see J. Katz and T. van Itallie, *Z. physik. Chem.*, **A150**, 90 (1930); also, J. Katz and J. Derksen, *ibid.*, **A167**, 129 (1933).

(4) (a) R. S. Bear and D. French, THIS JOURNAL, **63**, 2298 (1941); (b) A Frey-Wyssling, *Naturwissenschaften*, **28**, 78 (1940); *Ber. schweiz. botan. Ges.*, **59**, 321 (1940).

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

(6) In this paper we shall adopt the nomenclature of K. Meyer, "Rev. Colloid Science," Interscience Pub., Inc., New York, N. Y., p. 142. The unbranched component of starch will be referred to as "amylose."

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

(8) It is a point of importance that the amylose component in its various modifications gives the same diffraction patterns as whole starch. This observation would require that all points of branching be interruptions in the crystalline structure of starch. A critical examination of this observation will be reported in a subsequent paper.

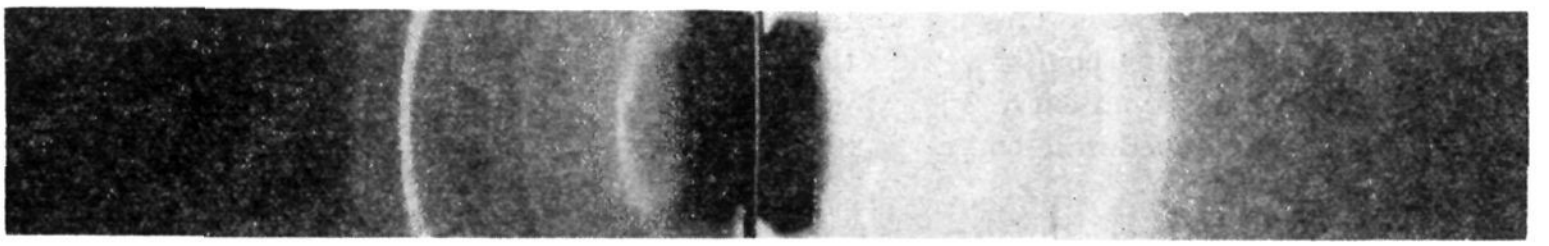

Fig. 1.—Powder diagram of the amylose–iodine complex: one-half of the diagram has been over exposed, the other half under exposed in printing in order to make visible as many diffraction maxima as possible at both large and small angles.

drying Schoch's butanol precipitated fraction over phosphorus pentoxide and staining with iodine vapor. The samples prepared in this way produced diffraction patterns far superior to those obtained from any other samples.

Iodine Absorption and Starch Configuration.—The method of preparing the amylose–iodine complex clearly illustrates the relation between the configuration of starch in its various modifications and the configuration of starch in the starch–iodine complex. Retrograded or granular starch, in either the "A" or "B" modification, is not stained by iodine vapor, or at most is tinted a light brown. Upon alcohol precipitation from solution starch assumes a different crystalline modification, the "V" modification.[3] It is found that starch or amylose in the "V" modification will absorb iodine vapor in quantity even when thoroughly dry.

Butanol appears to be superior to ethyl alcohol in preparing "V" starch samples. Schoch's butanol precipitate, when thoroughly dry, gives very excellent "V" diffraction patterns, and patterns very similar to the usual "V" pattern when wet with a saturated butanol solution. Either wet or dry the butanol precipitate will absorb iodine vapor rapidly. When dry it absorbs at least 26% of its own weight of iodine vapor. Dry butanol precipitates of corn, potato and lily bulb starch have been stained with iodine vapor. All three preparations produce the same X-ray diffraction pattern.

These experiments completely refute previous claims that iodide ion and/or water are necessary for starch–iodine complex formation.[9] Whatever role these substances play under other circumstances must be concerned chiefly with aiding the starch to assume the helical configuration which it lacks in the granule or in retrograded form.[4]

(9) (a) G. Barger, "Some Applications of Organic Chemistry to Biology and Medicine," McGraw-Hill Book Co., Inc., New York, N. Y., 1930, pp. 127–176; (b) K. Meyer and P. Bernfeld, *Helv. Chim. Acta*, **24**, 389 (1941).

Diffraction Patterns from the Amylose–Iodine Complex.—Diffraction powder patterns of the amylose–iodine complex were prepared with Ni filtered Cu K radiation using cylindrical cameras of both 5 and 10 cm. radius. Since there was considerable interest in finding weak reflections, a series of patterns was made with exposure time varied from a few hours to several days, until the background obscured observation of the reflections. The diagram in Fig. 1 was produced by an exposure of 500 ma. hours at 40 kv. peak.

Only three or four diffraction maxima from the amylose–iodine complex, Fig. 1, have been observed on previous diffraction patterns of the starch–iodine complex.[10] For these maxima, however, the patterns appear alike both in position and in relative intensity. Amylose–iodine patterns do not change appreciably with % iodine in the complex as long as the iodine content is fairly high, about 15%. A slight variation in the intensity of some reflections seems to accompany a change in the % iodine, but this is hard to establish.

The patterns are far richer than those previously reported[10] (Fig. 1), and are similar to, but simpler than, diffraction patterns from the dried butanol-precipitate. In Table I are listed all reflections which can be measured on the diffraction patterns obtained. The amylose–iodine pattern can be indexed using a hexagonal cell, $a_0 = 12.97$, $c_0 = 7.91$, $d_{100} = 11.23$ Å. All reflections of the type (h_1h_20) are quite strong, while all reflections of the type $(00h_3)$ are absent, and all reflections of the type $(h_1h_2h_3)$ are very weak. On patterns of low intensity only reflections (h_1h_20) are visible. It is to be noted that all possible reflections are found except at larger values of θ where the intensities of all reflections become very weak. Since c_0 is approximately equal to $d_{100}/\sqrt{2}$ many reflections of the type $(h_1h_2h_3)$ occur at nearly the same θ as the stronger reflections (h_1h_20). In such cases the observed

(10) R. S. Bear, THIS JOURNAL, **64**, 1388 (1942).

position of the reflection (h_1h_20) is probably not influenced by the superposition of the weaker reflection (Table I).

TABLE I

X-RAY POWDER DIAGRAM OF THE AMYLOSE–IODINE COMPLEX

Hexagonal indices	$\frac{\sin^2\theta}{\lambda^2}$ (obs.)	$\frac{\sin^2\theta}{\lambda^2}$ (calcd.)	Intensities
100	0.001965	0.001979	VS
110[a]	.005912	.005937[a]	S
101		.005965	
200	.007922	.007916	M
111	.009955	.009925	VW
201	.01158	.01192	VW
210	.01384	.01386	VS
300[a]		.01782[a]	
211	.01781	.01797	S
102		.01786	
301	.02189	.02182	VVW
112		.02193	
220[a]	.02375	.02375[a]	M
202		.02391	
310	.02573	.02573	MS
311	.02976	.02974	VW
212		.02985	
400	.03178	.03162	W
320	.03775	.03767	M
410[a]		.04158[a]	
321	.04155	.04166	M
312		.04174	
411	.04551	.04558	VVW
402	.04763	.04767	VVW
500	.....	.04950	nil
330	.05360	.05344	VW
420	.05549	.05542	VW
510	.06165	.06137	VW
600	.07114	.07126	VW
430	.07310	.07324	VW

[a] Only the reflection (h_1h_20) should be intense enough to influence the position of the line.

Discussion

From the rather meager data of a powder diagram it is difficult to make a straightforward attack on a structure as complicated as that of the amylose–iodine addition complex. The high symmetry of the structure is nevertheless very important in getting a rough picture of the structure. Indeed a hexagonal lattice for so complicated and unsymmetrical a substance as starch is hard to understand, unless the starch chains approximate cylinders which are then packed together in closest packing. The helical structure previously proposed provides an excellent mechanism for this packing.[2,11]

(11) Bear noted a spacing ratio of $\sqrt{3}$ for the first two observable reflections from "V" starch, in agreement with a hexagonal structure, and he discussed the possibility of helices.[10]

Freudenberg[12] has constructed a Stuart-type, space-filling model[13] of a starch helix using a "wannen" configuration for the pyranose ring in glucose. His helix contained six glucose residues per turn. Similar models can be built using a "sessel" form of the pyranose ring. In both cases the exterior diameter of the helix is within a few tenths of an Ångström of the 13 Å. required by the observed lattice translation. The length of a turn in the helix should be equal to the width of a glucose residue which, from the model, appears to be about 7.5 to 8 Å. The periodicity along the helix is found to be 7.91 Å. in good agreement. The observed cell dimensions are in full accord with a helix of six glucose residues per turn.

The "formula" for the starch–iodine complex has long been of interest. Previous work has been confined to preparation of the complex in solution[9a] where things other than iodine might take up room in the helix. For example, it has been shown that as the iodide concentration of a starch solution is increased the iodine which the starch can bind is decreased.[7] Further, most previous work has been carried out on whole starch. Since the amylose and amylopectin components of starch vary greatly in their complex formation with iodine,[7] work with whole starch is equivalent to work with a complex mixture.

The maximum iodine absorption by dry amylose appears to be about 26% of the weight of the amylose. This just corresponds to one iodine molecule for six glucose residues, or one iodine per turn in the helix. If this is correct, the amylose–iodine unit cell contains one iodine and six glucose residues. The theoretical density is then 1.76 g./cc. An experimental density is hard to determine. The material is porous, and any liquid, organic or inorganic, used in the usual density determination may extract iodine from the complex. Using ethylene dibromide–carbon disulfide solutions, no extraction of iodine was observed, and flotation of the complex gave a density of 1.69 g./cc. Since both porosity and extraction of iodine would lead to a low experimental result, this appears to be in satisfactory agreement with the theoretical density.

The formula for the complex is not entirely settled by the above considerations, however. Strong treatment with iodine vapor tends to de-

(12) K. Freudenberg, E. Schaaf, G. Dumpert, and T. Ploetz, *Naturwissenschaften*, **27**, 850 (1939).

(13) H. A. Stuart, *Z. physik. Chem.*, **B27**, 350 (1934).

compose amylose, and the value obtained for iodine absorption may be only a practical maximum and fortuitous. Packing considerations alone would allow about one iodine molecule for five glucose residues, since one molecule would require about 6.8 Å. along the helix. Furthermore, it is hard to understand why reflections of the type $(00h_3)$ are absent if the iodine molecules are spaced 7.91 Å. apart along the helix. It seems possible that their arrangement is at random in a set of six equivalent positions per turn in the helix, giving rise to an effective sixthing of the spacing along the c axis. Unfortunately, the temperature factor for the complex is so high that the reflection (006) could not possibly be observed at room temperature. This leaves the space group in doubt.

Summary

1. The amylose-iodine complex has a hexagonal unit cell, $a_0 = 12.97$, $c_0 = 7.91$, $d_{100} = 11.23$ Å.

2. The unit cell confirms a helical structure for the starch–iodine complex; 12.97 Å. is the diameter of the helix, 7.91 Å. is the length of a turn in the helix. These dimensions are in good agreement with the dimensions of a space-filling model of a helix with six glucose residues per turn.

3. The starch–iodine complex can be prepared entirely without water or iodide ion if the starch is first put in the "V" configuration by alcohol precipitation.

4. Starch in the "V" configuration will absorb iodine vapor in quantity, while in the "A" and "B" configuration it will not. Amylose in the "V" configuration will absorb 26% of its own weight in iodine. This corresponds to one iodine for six glucose residues, but it is not established that this is the maximum iodine absorption.

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

End Group Structure of Polyvinyl Alcohol[1]

BY C. S. MARVEL AND G. ESLER INSKEEP

The recurring unit in polyvinyl alcohol has been shown to be that indicated in Formula I and the

$$\left[\text{-CH}_2\text{OH-}\right]_n$$
$$\text{OH}$$

I

chemical behavior of the polymer is in general that which would be expected of a poly-1,3-glycol.[2] However, Staudinger and Warth[3] have found that alcoholysis of a given polyvinyl acetate by different methods produces specimens of polyvinyl alcohol having different properties. Blaikie and Crozier[4] have noted unusual changes in viscosity in polyvinyl acetate samples on hydrolysis and reacetylation. Also they have found that mineral acid causes polyvinyl alcohol to become insoluble. McDowell and Kenyon[5] have found that saponification of polyvinyl acetate by alcoholic potassium hydroxide followed by reacetylation by means of acetic anhydride and pyridine usually results in a reduction of chain length as measured by viscosity methods, by about one-half. Industrial experience[6] with these compounds has shown also that unusual molecular weight changes, based on viscosity determinations, on hydrolysis of polyvinyl acetates or acid treatment of polyvinyl alcohols, are not uncommon.

In the present communication are described some experiments on the hydrolysis of polyvinyl acetate samples and acid treatment of various polyvinyl alcohols in which the chain lengths measured by viscosity methods show marked changes. These changes may be in either direction depending on experimental conditions.[7]

Viscosity molecular weights and degrees of polymerization were calculated by means of the Staudinger equation using a K_m value of 2.6×10^{-4} for both polyvinyl acetate in benzene and polyvinyl alcohol[8] in water containing 2% ethanol. To solutions of polyvinyl alcohol which contained

(1) This is the sixteenth communication on the structure of vinyl polymers. For the fifteenth, see THIS JOURNAL, **65**, 1647 (1943).

(2) Staudinger, Frey and Stark, *Ber.*, **60**, 1782 (1927); Herrmann and Haehnel, *ibid.*, **60**, 1658 (1927); Marvel and Denoon, THIS JOURNAL, **60**, 1045 (1938).

(3) Staudinger and Warth, *J. prakt. Chem.*, **155**, 261 (1940).

(4) Blaikie and Crozier, *Ind. Eng. Chem.*, **28**, 1155 (1936).

(5) McDowell and Kenyon, THIS JOURNAL, **62**, 415 (1940).

(6) Private communication from Dr. B. C. Bren.

(7) The samples of polyvinyl acetate and polyvinyl alcohol were kindly furnished by Dr. B. C. Bren of the Plastics Department, E. I. du Pont de Nemours and Company, and we are indebted for his aid.

(8) Staudinger and Schwalbach, *Ann.*, **488**, 8 (1931).