

THE EFFECTS OF VARIOUS EXPERIMENTAL
FACTORS UPON THE LIQUID PHASE
CHLORINATION OF STARCH

by

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INTRODUCTION

Starch is one of the most abundant and most nearly inexhaustible sources of raw organic material available to mankind. In contrast to closely related cellulose and other important organic raw materials which have yielded a multiplicity of industrially important derivatives, starches are used merely as slightly modified forms.

Much work has been carried out in recent years in an attempt to better utilize this vast reservoir of raw material by converting it into industrially feasible derivatives. Such derivatives naturally would give impetus to the growth of many starch bearing crops which are especially adapted to the Midwest, and which have been used in the past merely as feed crops. However, with the exception of some ethers and esters which are of little industrial importance, few derivatives of starch have been known until recently.

In 1942, intensive work was begun in this laboratory on the liquid phase chlorination of starch (1). This work resulted in products containing one, two, three, four, and six chlorine atoms per glucose unit (2); however, only the products through the trichloride appeared to retain the granular structure of the original starch. Conditions for the formation of the monochloride and dichlorides were well established, but success in forming the granular trichloride was

attained only once.

The work reported in this thesis deals with a study of the conditions believed necessary for the formation of the trichloride.

LITERATURE SURVEY

References to the chlorination of starch with liquid chlorine are rather limited since the only reported work of this nature has been conducted in this laboratory. Many cases have been reported in which gaseous chlorine or aqueous hypochlorites have been used to effect physical changes in starch, but these have not produced any derivatives containing significant amounts of bound chlorine.

Beutel and Kutzelnigg (3, 4) carried out reactions between cellulose and liquid bromine, liquid chlorine, iodine, and iodine chloride. They noted that in the bromination reaction a large excess of bromine was needed to prevent carbonization of the product. Barham and Thomson (1) later found this to hold true for the reaction between starch and liquid chlorine.

The work which was done upon the direct chlorination of starch in liquid chlorine from 1939 to 1947 was reported by Barham and Thomson (1, 2). Evidence was presented in support of a proposed mechanism of reaction, and of the probable structure of the products. Stickley (5) later reported upon

the chlorination of a solvent extracted cornstarch in liquid chlorine.

NATURE OF PROCESS AND PRODUCTS

It has been shown that anhydrous granular starch will react with a suitable excess of liquid chlorine at temperatures from 55° to 80° to form derivatives containing one, two, and three atoms of bound chlorine per glucose unit. At temperatures of from 90° to 125° , derivatives may be obtained containing four, five, and six chlorine atoms per glucose unit. It has been found that a molar ratio of chlorine to hydrogen chloride greater than 6:1 must be maintained until the product has reached the monochloride stage; otherwise an uncontrolled reaction occurs which results in complete carbonization of the starch. There is evidence to indicate that this deactivation of a hydrogen chloride molecule by six molecules of chlorine is due to complex formation.

In order to determine the extent of chlorination of a product, analyses are made of the amount of hydrogen chloride formed and of the amount of bound chlorine in the product. The results of these analyses are expressed as the number of equivalents per glucose unit, and are designated as HCl_g and Cl_g . The ratio between these two quantities varies contin-

uously during a reaction and approaches stoichiometric proportions only at certain stages. The ratio, then, is indicative of a series of reactions, so neither value alone suffices to describe the extent of reaction. Thus, for example, a reaction may be described as a (3:1) reaction, indicating that three moles of hydrogen chloride have been evolved per glucose unit and one atom of chlorine has become bound.

The chlorination reaction occurs in three stages. The first of these is an induction period, usually several hours in length, during which the starch gradually turns black. Practically no chemical reaction occurs at this stage. At the end of the induction period, a sudden increase in reaction rate occurs, during which a monochloride is formed, and the starch changes to a pale yellow. After completion of the monochloride stage, the rate of reaction decreases rapidly, and the third stage is initiated during which the higher chlorinated products are formed.

In order to determine the probable structure and composition of a chlorinated product, the adsorbed gases are removed by holding the product for 24 hours at 0° C. and five mm of mercury. The "degassed" product thus obtained contains chemically bound oxidizing groups, provided chlorination has proceeded beyond the end of the induction period. The amount of oxidizing groups may be determined by reduction with iodide ions in aqueous acid media. Heating of the degassed product for 24 hours at 70° and under a pressure of five mm

of mercury causes an evolution of hydrogen chloride and chlorine, and the loss of most, but not all, of the oxidizing power.

Analytical data obtained by the pyrolysis show that three different types of intermediate structures are present in the degassed products; (1) an oxidizing group which may decompose to yield a molecule of hydrogen chloride, (2) an oxidizing group which decomposes entirely to yield a molecule of chlorine, and (3) a nonoxidizing group which decomposes to yield a molecule of hydrogen chloride.

From considerations such as the above, it has been assumed that the following single-carbon structural groups are present during the chlorination process.



I. Carbinol



II. Chloro-carbinol



III. Hypochlorite



IV. Chloro-hypochlorite



V. Carbonyl



VI. Carbon-bound hydrogen



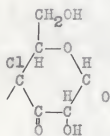
VII. Carbon-bound chlorine

Structures I to V, inclusive, are the structures which are possible for carbons two, three, and six of the glucose

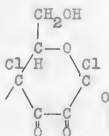
unit. Structures I and VI are present in the original starch. Carbons one, four, and five may have the structures represented by VI and VII.

The pyrolyzed products have been found to contain an oxidizing group, and in keeping with general chemical knowledge in regard to the stabilities of the various possible groups, it has been concluded that the hypochlorite is the only group stable enough to remain.

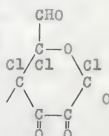
The positions of the various structural units were assigned after considerable study of the kinetics of the reaction and of the spatial configuration of the starch granule. It was upon this basis that the following structures were assigned.



Monochloride



Dichloride



Trichloride

The α -dicarbonyl structure of the dichlorides and trichlorides is substantiated by their reactions with o-phenylene-diamine in alcoholic solutions to form dark brown quin-oxaline derivatives, and also by the intense yellow color of the products, which is typical of the α -dicarbonyl group. The trichlorides react rapidly with Fuchsin-aldehyde reagent

whereas the dichlorides react only after several minutes. This supports the aldehydic structure of the trichloride.

EXPERIMENTAL PROCEDURE

Prior to each chlorination, the starch sample was adjusted to the desired moisture level. In most of the experiments, catalytical amounts of water were left in the starch by drying it to the desired moisture content over concentrated sulfuric acid in a vacuum desiccator. In some of the experiments, however, completely dry starches were used. These were prepared by drying overnight in a vacuum oven at 110°C .

After the desired moisture level had been attained, the starch sample was weighed into a tared glass liner which then was placed into a specially constructed autoclave. The autoclave was then closed off and evacuated by means of a mechanical vacuum pump and allowed to cool to -20°C . A complete description of the autoclave used in this work is given by Barham and Thomson (2).

The chlorine was distilled into the chilled autoclave using a five-foot length of flexible seamless stainless steel tubing (1/16 in. I.D. and 1/8 in. O.D.) to connect the chlorine tank to the autoclave. The cooling of the chlorine tank due to the distillation was off-set by means of a specially constructed Glas-col electric heater jacket which was fitted

around the chlorine tank. Current to the heater was regulated by means of a variac. The amount of chlorine delivered into the autoclave was determined by loss in weight of the cylinder during the transfer. For the experiments described in this paper, 450 grams of chlorine were used.

When the desired amount of chlorine had been distilled into the autoclave, it was placed inside its heater jacket, and heating and shaking were started. The rate of heating was adjusted manually until the desired reaction temperature was reached, after which the temperature was maintained by a Wheelco Potentiostat. The control element for the Potentiostat was an iron-constantan thermocouple which was inserted into a thermo-well at the base of the autoclave. When the desired reaction time was completed, the autoclave was removed from the heater jacket and cooled to -20°C . as quickly as possible to quench the reaction.

The length of each reaction was measured from the time at which the autoclave reached the desired reaction temperature to the time when the autoclave was removed from the heater jacket. In this manner, all reaction times were expressed on a relative basis.

When the autoclave was considered chilled sufficiently to stop all further reaction, it was removed from the refrigerated room and the gases which it contained were discharged slowly through two water filled gas washing bottles fitted with fritted glass disks to ensure thorough scrubbing

of the effluent gases. When the pressure within the autoclave reached one atmosphere, two smaller gas washing tubes were attached to it. These, in turn, were connected to a vacuum pump. The first tube contained water to fix the remaining hydrogen chloride, and the second tube contained a 10 per cent aqueous solution of sodium hydroxide to fix the remaining gaseous chlorine and prevent its entry into the vacuum pump. The pressure within the autoclave was reduced to about five mm of mercury, maintained there for 15 minutes, and then slowly restored to atmospheric pressure. The water scrubs were combined, diluted to one liter, and then analyzed for hydrogen chloride. The autoclave then was opened, and the tared liner was weighed to determine the increase in weight of the product. Preparatory to the removal and estimation of the amount of adsorbed chlorine and hydrogen chloride, the product was placed in a tared 125 ml Erlenmeyer flask with a 24/40 standard taper neck, and the weight of the flask and contents was determined. The flask was placed in an ice filled Dewar flask, and connected to two gas washing tubes. The first tube contained about 125 ml of water to fix hydrogen chloride, and the second contained 10 per cent aqueous sodium hydroxide to fix chlorine. Both tubes were also immersed in ice filled Dewar flasks. The second tube was connected to a bubble counter, filled with sulfuric acid, and the bubble counter was connected to a vacuum pump which was protected by a tube packed with alternate layers of

sodium hydroxide and calcium chloride. The pressure within the system was reduced to five mm of mercury and held there for 24 hours.

At the end of the degassing period, pressure was restored to normal, and the flask containing the product was removed, washed with absolute ethanol, wiped with a clean cloth, and dried in a desiccator for 30 minutes prior to weighing. The loss of weight of the product was then determined, and a sample was removed for analysis. The water scrub was removed from the ice bath and diluted to 500 ml in a volumetric flask. It was analyzed for hydrogen chloride.

Pyrolysis of the product was conducted in much the same manner as the above operation. The tared flask and weighed product were placed in an oil bath maintained at 70° C. For the pyrolysis, however, no water scrub was used. Instead, the gaseous products of the pyrolysis were passed through a single gas washing tube containing about 125 ml of 10 per cent aqueous sodium hydroxide. This tube, in turn, was connected to a bubble counter and vacuum pump as used in the degassing procedure. The sodium hydroxide solution was maintained at 0° C. by means of a Dewar flask filled with crushed ice. The pressure within the system was then reduced to 5 mm for 24 hours. At the end of the pyrolysis period, the pressure in the system was restored to normal, and the flask containing the pyrolyzed product was cleaned with petroleum ether, cooled in ice water, washed in absolute ethanol,

and dried in a desiccator for 30 minutes prior to weighing. The loss in weight was a measure of the amount of intermediate structures which had decomposed and had been carried over into the sodium hydroxide scrub tube. The basic scrub solution then was removed and diluted to 500 ml in a volumetric flask. It was analyzed for sodium hypochlorite and total chlorine content. The difference between the two values was a measure of the amount of hydrogen chloride which had been formed during pyrolysis, and the amount of sodium hypochlorite was a measure of the amount of chlorine which had been formed during pyrolysis. Both the degassed and pyrolyzed products were analyzed for bound chlorine by fusion with sodium peroxide and precipitation of the chloride ions with silver nitrate.

RESULTS AND CONCLUSIONS

The first reported formation of the starch trichloride was achieved by the use of a temperature gradient starting at 30° C. The moisture level of the cornstarch which was chlorinated was 0.39 per cent. Other experiments had previously shown that cornstarch gave no appreciable reaction with liquid chlorine below 55°. The success of the experiment indicated that the catalytic amount of water under the conditions present in the autoclave below 55° was able to disrupt the extensive pattern of hydrogen bonding to such an

extent that certain functional groups were made available for reaction. This consisted, essentially, of freeing the primary hydroxyl group. The present work was started on this basis.

A series of experiments designated as GF-3 through GF-12 was begun on October 3, 1950 to determine the kinetics of a reaction between cornstarch No. 10 and liquid chlorine using a temperature gradient. Fifty degrees centigrade was chosen as the starting temperature, and a moisture level of approximately 0.5 per cent was used in all samples prior to chlorination. The reaction proceeded as shown in Fig. 1. It soon became obvious that cornstarch No. 10 was a relatively unreactive starch. Several attempts were made to increase the reactivity, but no appreciable success was attained. It was thought possible that the extraction of the lipids from cornstarch with ammonium hydroxide might leave the surfaces of the granules much more porous than in the native starch. Chlorination of a sample of cornstarch No. 10, designated as experiment GF-20, which had been extracted with concentrated ammonium hydroxide, resulted in a product with a smaller percentage of bound chlorine than was obtained by chlorinating untreated cornstarch No. 10 under the same reaction conditions. Removal of the lipids from the granular surfaces apparently was attended by a second change which resulted in a diminution of the size of the surface openings.

Another suitable approach to the problem seemed to be to solvent extract the starch with hot methanol according to the

Table 1. Data for kinetic analysis of the liquid phase chlorination of cornstarch No. 10.

Experiment number:	Reaction schedule : degrees C. :	Reaction schedule : in days :	Degassed product : HClg : Clg : HClg/Clg :			Pyrolyzed product : HClg : Clg : HClg/Clg :			Per cent moisture
GF-3	50	5	.159	.036	4.37	.159	.036	4.51	0.54
GF-4	50/55	5/2	.136	.106	1.54	.163	.106	1.54	0.42
GF-5	50/55	5/4	.243	.176	1.38	.243	.009	2.45	0.48
GF-6	50/55/60	5/4/2	.322	.287	1.12	.333	.195	1.71	0.47
GF-9	50/55/60	5/4/3	2.583	.753	3.43	2.751	.569	4.83	0.66
GF-12	50/55/60	5/4/3 $\frac{1}{4}$	3.807	2.135	1.78	3.973	1.673	2.37	0.46
GF-10	50/55/60	5/4/4	4.085	2.481	1.65	4.299	1.970	2.18	0.42
GF-8	50/55/60	5/4/5	4.238	2.067	2.05	4.352	1.612	2.70	0.65

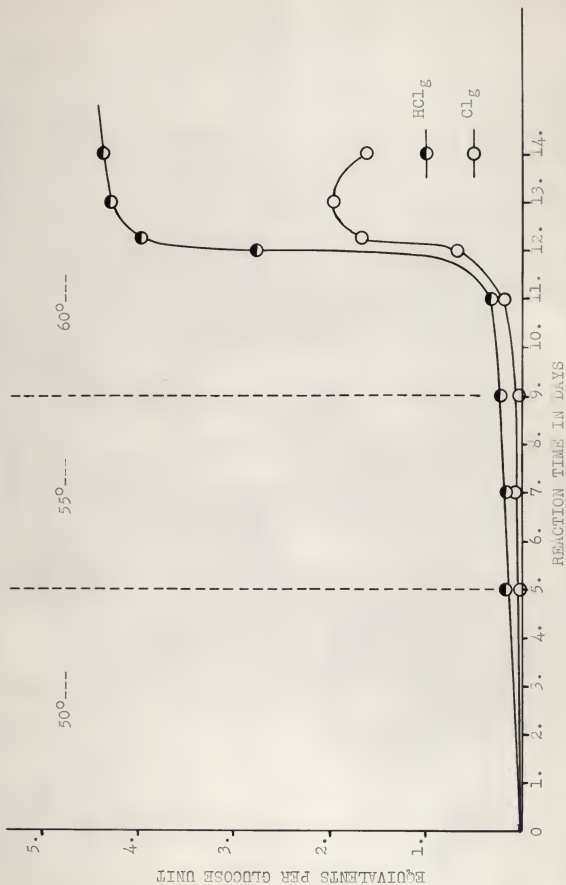


Fig. 1. Molecules of HCl evolved and atoms of bound chlorines, per glucose unit, for the pyrolyzed products.

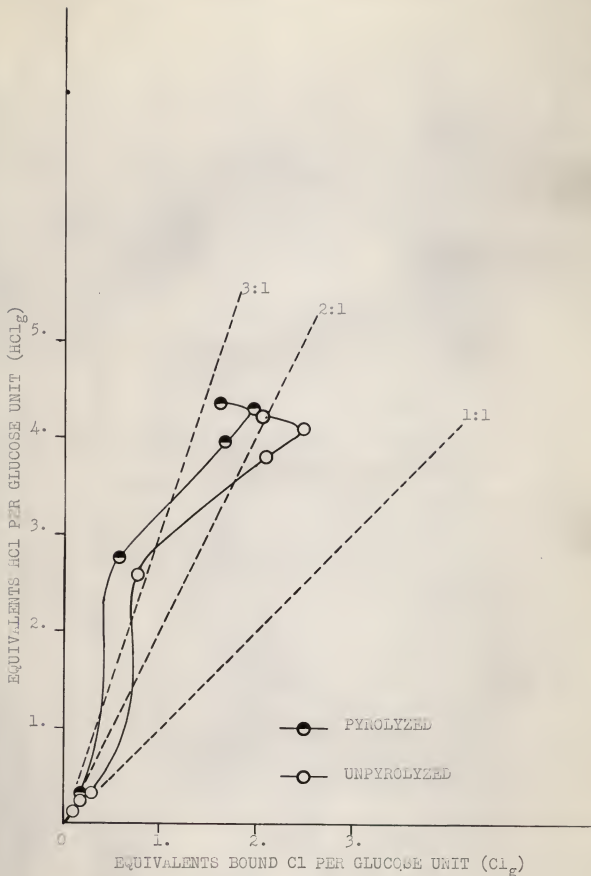


Fig. 2. Effect of pyrolysis at 70° on mechanism curve.

method of Schock (6) prior to its chlorination. The resultant product, however, contained slightly less chlorine than the product formed from the ammonium hydroxide extracted starch.

It is generally recognized that ordinary cornstarch consists of α -D-glucose units joined primarily through 1,4-ether linkages; however, approximately four per cent of the gross structure consists of 1,6-ether linkages. Recent work by Barham* emphasizes the possibility that most of the 1,6-ether linkages occur in the surface of the granules. The chlorination of such a surface structure would very likely proceed at a much greater rate than the chlorination of the interior structure. The result would be a replacement of small hydrogen atoms in the surface lattice of the granule with large chlorine atoms, and of course the porosity of the surface would be considerably diminished. Removal of the lipid material from the granular surfaces would probably accentuate this effect; however, the rate of chlorination of the surface structure should not be assumed to be the sole factor governing the availability of chlorine to the interior of the granule since both ammonium hydroxide extraction and methanol extraction have been shown to produce marked changes in the pasting characteristics of starches. These effects of extraction upon pasting characteristics have been interpreted

* Personal communication of unpublished data from this laboratory.

as being due to structural changes in the surfaces and within the granules. Evidently, extraction of a starch results in an increase in the amount and extent of hydrogen bonding within the granule, and the increased degree of structuralization is reflected in the rate of chlorination. The chlorination reaction, then, may be considered as a function of the rate of the availability of the functional groups as determined by the granular surface or the internal structure or both.

Since very little progress had been made toward the formation of the trichloride, a slightly different approach to the problem was tried. The dichloride obtained from experiment GF-44 was re-chlorinated in experiment GF-51. It was reasoned that the intermediate structural units such as the chlorocarinol and chlorohypochlorite which were formed during the first chlorination occupied favorable positions in the walls of the helices. When such structures were broken down during pyrolysis, it seemed probable that new avenues of approach to the primary carbinol groups located on the outer walls of the helices would result. The product of experiment GF-51 seemed to substantiate this view to a certain extent since a large increase in the carbonyl content was observed; however, the amount of bound chlorine increased only slightly, indicating that carbons five and six were still protected.

The experiments designated as GF-39, GF-42, and GF-43 were chlorinations of South African kafir, San Domingo

Table 2. Chlorination data.

Experiment: number	: temperature: degrees C.:	Reaction: time : in hours:	Degassed product		Pyrolyzed product	
			Mole wt.	: per cent : chlorine	Mole wt.	: per cent : chlorine
GF-19	70	72	230.69	31.65	218.03	27.78
GF-20	70	72	218.06	27.57	212.37	25.69
GF-21	70	72	214.33	26.33	210.17	24.92
GF-39	70	72	227.82	30.80	215.57	27.01
GF-42	70	72	162.14	0.00	-	-
GF-43	70	72	245.37	35.54	223.50	29.79
GF-44	70	72	220.47	28.98	211.99	26.22
GF-51	80	48	221.73	29.83	214.99	27.65
GF-56	70	72	231.19	31.90	-	-
GF-57	80	72	242.73	35.69	231.20	32.52
GF-59	70	72	241.00	34.53	219.57	28.19
GF-61	80	72	245.50	37.45	232.64	32.96
GF-60	70/80	72/72	254.41	38.80	244.98	36.50
GF-62	70	72	241.58	34.81	-	-
GF-63	80	72	249.42	37.68	239.27	35.07

Table 2. (concl.)

Experiment number:	Degassed product			Pyrolyzed product			Per cent moisture
	HCl : g	Cl ₂ : g	HCl : g / Cl ₂ : g : Carbonyl : g	HCl : g	Cl ₂ : g	HCl : g / Cl ₂ : g : Carbonyl : g	
GF-19	4.423	2.059	2.15	1.182	4.638	1.708	0.48
GF-20	4.157	1.696	2.44	1.231	4.299	1.539	0.48
GF-21	4.200	1.597	2.63	1.304	4.315	1.477	0.41
GF-39	4.463	1.980	2.26	1.242	4.725	1.642	0.53
GF-42	none	-	-	-	-	-	0.50
GF-43	5.249	2.440	2.15	1.405	5.340	1.875	0.39
GF-44	5.513	1.802	3.06	1.856	5.688	1.568	1.74
GF-51	6.500	1.865	3.48	2.317	6.645	1.677	none
GF-56	4.644	2.080	2.24	1.292	-	-	0.51
GF-57	6.004	2.443	2.46	1.785	6.073	2.121	none
GF-59	4.313	2.347	1.84	0.983	4.427	1.746	*
GF-61	6.028	2.635	2.28	1.697	6.104	2.162	none
GF-60	6.591	2.784	2.30	1.803	6.518	2.522	*
GF-62	4.628	2.372	1.95	1.128	-	-	*
GF-63	6.651	2.651	2.51	2.001	6.742	2.367	none
						2.84	

* Dried in vacuo at 110°.

tapioca, and Westland X Cody sorghum starches, respectively, and were attempts to find a starch having a higher initial reactivity. Of the three, the Westland X Cody proved the most reactive, and its dichloride was re-chlorinated in experiment GF-53. The product of the re-chlorination had a high chlorine content, but due to experimental difficulties, part of the gases produced during the reaction were lost so the amounts of bound chlorine and hydrogen chloride evolved could not be calculated; however, the per cent of bound chlorine in the pyrolyzed product was still far short of the desired trichloride.

Experiments GF-56 and GF-57 were carried out to determine the effect of re-chlorinating a degassed dichloride made from the Westland X Cody starch. The results, as shown in Table 2, indicate very little progress beyond the dichloride stage.

It was finally concluded that the catalytic amounts of water employed in all of the experiments up through GF-57 yielded no perceptible beneficial results. This could be explained by assuming that the small amounts of moisture present in the starches were not in positions which would enhance the reactivities upon cleavage of hydrogen bonds. Experiments GF-59 through GF-63 were carried out using samples of Westland X Cody starch which had been dried in vacuo at 110° .

Experiments GF-59 and GF-61 were conducted to determine the effect of forming a dichloride from a completely dry starch, degassing and pyrolyzing, and then re-chlorinating the pyrolyzed product at a higher temperature. Experiment GF-60 was conducted to compare the effect of chlorinating an identical sample at the same reaction temperatures and for the same periods of time, but without stopping the reaction until the total time had elapsed. Experiments GF-62 and GF-63 were conducted to determine the effect of forming a dichloride from a completely dry starch, degassing only, and then re-chlorinating the degassed product.

It is apparent from the data of Table 2 that when the product was removed and pyrolyzed, a decrease in the reactivity was produced. Thus it seems that decomposing and removing the unstable intermediate structures from their positions within the walls of the helices under the conditions employed for pyrolysis allowed the helices to assume a more compact and stable configuration. On the other hand, the results indicate that when the intermediate structures were decomposed in the reaction chamber the helices had no chance to assume a more stable configuration because the chlorine which was present was able to immediately penetrate the micelle walls, at least to a certain extent. That this extent was limited is shown by the small amount of hydrogen chloride evolved beyond the dichloride stage. Apparently only one hydrogen from carbon five or six was involved to any

great extent. Removal of the dichloride formed in experiment GF-62 and degassing prior to re-chlorination apparently induced a slightly different course of reaction as indicated by the increased amount of hydrogen chloride formed in experiment GF-63. Notable also is the increase in the amount of carbonyl structure. Essentially, the main difference between the formation of products GF-61 and GF-63 was that all hydrogen chloride was removed from the reaction medium prior to completion of the latter half of the reaction for GF-63. Since it has been shown that one molecule of hydrogen chloride forms a complex with six molecules of chlorine, it seems very probable that the hydrogen chloride formed during the early part of the reaction resulted in a slight decrease in the availability of chlorine at the reactive centers within the granules. The results of experiment GF-63 also indicate that a more extensive reaction with carbons five and six occurred. This is shown by the comparatively large amount of carbonyl structure formed.

One thing which should be emphasized was the marked difference in reactivity between cornstarch No. 10 which was a nonglutinous starch, and the Westland X Cody, which was a glutinous type of starch. Examination of the pasting characteristics of cornstarch No. 10 and of the iodine sorption behavior of the Westland X Cody (7) revealed that both starches were inhibited, indicating rather tight surface structures. On the other hand, a comparison of the chlori-

nation data from both starches suggests the possibility that even though the granular surfaces of the Westland X Cody were restricted, they possessed some type of structure which was able to undergo a stretching action as the chlorine diffused into the inner regions of the granules. The granular surfaces of the cornstarch were in a restricted state initially, and seemed to remain so. Studies of pasting characteristics have also indicated that glutinous type starches have a much less integrated type of internal structure, which would seem to allow more complete diffusion of chlorine throughout the granule prior to reaction. Apparently, both conditions combined to increase the extent of chlorination of the glutinous type of starch.

The failure to form a trichloride similar to the one reported by Barham and Thomson (1) may have been due to the difference in the temperature gradients used. The low initial temperature used in the successful work may have been able, with the aid of the catalytic amount of water employed, to cause structural changes in the granular surfaces. In this manner, the original rather rigid surface structure was changed to a more elastic type structure which would make the granular interiors much more accessible to the chlorinating medium.

Needless to say, the results of the entire study were somewhat disappointing as the desired goal of formation of the (9:3) trichloride was not attained; however, it is hoped

that a worthy contribution has been made. It is the opinion of the author that, in the light of recent developments in this laboratory, information may soon be available to provide a solution to the problem.

SUMMARY

The kinetics of the reaction between cornstarch No. 10, containing a catalytic amount of water, and chlorine were determined in an effort to find the conditions necessary for the formation of the trichloride. Cornstarch No. 10 was found to be relatively unreactive, so several pretreatments were tried in attempts to increase the reactivity.

Extraction with both ammonium hydroxide and hot 85 per cent methanol resulted in decreased reactivity. From this, and considerations of the pasting characteristics of extracted starches, it was concluded that the chlorination reaction may be considered as a function of the rate of the availability of the functional groups as determined by the granular surface or the internal structure or both.

Re-chlorination of samples of dichlorides made from cornstarch No. 10 resulted in large increases in the carbonyl content, but the amounts of bound chlorine remained low. Cornstarch No. 10 was finally discarded because of its unreactivity.

Westland X Cody sorghum starch was found to be fairly

reactive, and re-chlorination of its dichlorides resulted in products having rather large amounts of bound chlorine and carbonyl structures; however, the most reactive samples were obtained by first removing all moisture by drying in vacuo at 110° . It was also found that a slight decrease in reactivity of the dichlorides were produced by removing and pyrolyzing the dichloride prior to re-chlorination, and an increase in reactivity was produced by removing and degassing prior to re-chlorination.

The marked difference between the reactivities of corn-starch No. 10 which was a nonglutinous starch and the Westland X Cody which was a glutinous starch was believed to be due to some type of structure in the surface of the glutinous starch which was able to undergo a stretching action as the chlorine diffused into the granules, and also to a less integrated internal structure which would seem to allow more complete diffusion of the chlorine throughout the granules.

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AN ABSTRACT

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The purpose of the work was to study the effects of various experimental factors such as time, temperature, and varied pretreatments upon the reaction between starch and liquid chlorine in an attempt to find a means of forming the starch trichloride.

All reactions were carried out in a specially constructed autoclave which was heated and stirred by means of a rocking heater jacket. At the end of each reaction, the autoclave was chilled thoroughly, and the gaseous products of the reaction were removed and determined. The product was then removed, degassed for a period of 24 hours at zero degrees centigrade and five mm of mercury, and then pyrolyzed for 24 hours at 70°C and five mm of mercury. The amount of bound chlorine and the amount of hydrogen chloride evolved per glucose unit were then determined.

First, the kinetics of the chlorination of a cornstarch containing a catalytic amount of moisture of the order of 0.5 per cent were studied, but no perceptible beneficial results were obtained. Extraction of the same cornstarch with both concentrated ammonium hydroxide and hot methanol resulted in a decrease in the extent of chlorination. This was thought to be due partly to an increase in the rate of chlorination of the surface structure due to removal of the lipid material from the granular surfaces. This, in turn, apparently resulted in a decrease in the porosity of the granular surfaces. Previous work has indicated that extraction causes an increase in the degree of structuralization. This, also, was thought to play an important role in the decreased extent of chlorination.

An attempt was made to increase the extent of chlorination by first forming a dichloride from a cornstarch, degassing and pyrolyzing, and then rechlorinating the pyrolyzed product. A large increase in the carbonyl content of the final product was observed, but the amount of bound chlorine increased only slightly. A Westland X Cody sorghum starch proved to be a much more reactive starch than the cornstarch, and rechlorination of dichlorides formed from the Westland X Cody resulted in large increases in the amounts of bound chlorine and of carbonyl structure; however, no product reached the trichloride stage.

Previous work had shown that both starches were inhibited, indicating rather tight surface structures; however, the chlorination data suggests the probability that the granular surfaces of the Westland X Cody, which was a glutinous type of starch, possessed some type of structure which was able to undergo a stretching action as the chlorine diffused into the granules. The granular surfaces of the cornstarch, which was a non-glutinous starch, were in a restricted state initially, and seemed to remain so.