

THE ACTION OF ACETIC ACID ON THE
DICHLORIDES OF STARCH

by

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Table of Contents

	Page
INTRODUCTION	1
REVIEW OF LITERATURE	3
METHODS	5
Preparation of dichlorides	5
Degassing and pyrolysis	6
Structure analysis	8
Acetylation	10
RESULTS AND DISCUSSION	16
Structure analysis	16
Acetylation	17
SUMMARY	29
ACKNOWLEDGMENTS	31
LITERATURE CITED	32
APPENDIX	33

INTRODUCTION

The history of starch can be traced almost to the beginning of civilization. Its uses are many, and its value to mankind is unquestioned. Its manner of storage by the plant in roots, fruits, and seeds makes it easily obtainable in a relatively pure form. Of the many purposes for which starch is utilized, some make use of the physical properties peculiar to the substance, such as its ability to swell and paste when placed in warm water. Others depend on the ability of the long starch molecules to undergo hydrolysis to the simpler glucose units, as in the preparation of syrups. It has been realized in recent years that the value of starch would be greatly enhanced if it were possible to modify the chemical structure of the glucose units of the starch molecule without allowing hydrolysis of the connecting ether linkages to occur. The high polymeric nature of the starch molecule suggests the preparation of plastics, while the various degradation products which could be obtained might be of value as intermediates for the synthesis of commercial chemicals.

As the first step toward this goal, it was desired to bring into the starch molecule atoms or groups of atoms which would lend themselves readily to the production of valuable derivatives and plastics. From a practical as well as a theoretical standpoint, chlorination was selected as the key to the starch molecule. The reaction has been carried out successfully in this laboratory, the mono-, di-, tri-, tetra-, and hexachlorides having been prepared (2, 3, 9). There now follows the necessity of determining the physical and chemical nature of these chlorides before intelligent

use can be made of their properties.

The ease of preparation and stability of the dichlorides have made them the preferred choice for preliminary studies, and it is with the dichloride that this work is concerned. The following structure has been assigned to this compound by Barham and Thomson (2, 9).

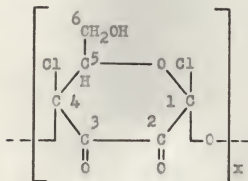


Fig. 1. The glucose unit of starch dichloride.

The value of x is assumed to be of the same order as that of the original starch (9). This structure no longer represents the original glucose unit of starch, since it has been chemically changed through oxidation as well as chlorination, but for convenience it has been designated as the glucose unit of the dichloride of starch. The carbon atoms are numbered in accordance with the original glucose structure to facilitate discussion.

The utility of these chlorides is, to a certain extent, determined by the ease of controlled replacement of the chlorine atoms by other atoms or groups of atoms. It is desired to show by this investigation the existence and extent of the replacement of the chlorine atoms of the dichloride of starch by the acetate group under various imposed reaction conditions.

REVIEW OF LITERATURE

There is no record in the literature of the preparation of the chlorides of starch except that which has been contributed by this laboratory. Barham, Stickley, and Caldwell (1) reported the successful chlorination of starch with phosphorous pentachloride in 1946, and the direct chlorination of starch with liquid chlorine as carried out by Barham and Thomson (2, 9) is soon to be published.

The thesis submitted by Thomson (9) in partial fulfillment of the requirements for his doctor of philosophy degree is a rich source of information concerning not only the preparation of the starch chlorides but also some of the preliminary studies of their physical and chemical properties.

Thomson (9) indicated that it was quite probable that the chlorine atoms on carbons 1 and 4, Fig. 1, differed considerably in stability. As supplementary evidence, Bryske (5) reported that one of the chlorines was not removed by saponification with sodium hydroxide in the cold. Thomson (9) also reported that the dichloride of starch, which he found to be insoluble in glacial acetic acid, when heated with the acid suddenly swelled and coagulated to yield a yellow precipitate containing about half the original chlorine. This he attributed to the replacement of the chlorine on carbon 1 by the acetate group. His choice of the chlorine on carbon 1 as the more unstable was supported by the fact that a chlorine in that position would be in essence an acid chloride, since that carbon is attached to two oxygen atoms through ether linkages.

Further investigation by this laboratory (3) was designed to elucidate the reaction of acetic acid and starch chlorides. In ad-

dition to carrying out the coagulation reaction indicated above, a sample of a dichloride (29.20 per cent chlorine) was refluxed with glacial acetic acid for six hours. A soluble and insoluble fraction resulted, and the chlorine analysis of the two fractions gave 20 per cent chlorine for the soluble portion and 16 per cent chlorine for the insoluble portion. The conclusions drawn from these experiments were that the rapid precipitation of the dichloride by boiling for a few minutes in glacial acetic acid converted the dichloride to the monochloride (whose structure was not quite clear), that the two chlorines were quite different in stability, and that prolonged heating (six hours) resulted in two fractions of different chloride content. It was further suggested that the insoluble portion might be justified on the basis of partial esterification of the primary alcohol group.

Barnes and Tulane (4) reported they had experienced difficulty in obtaining acetylation of α -halo diketones using fused sodium acetate in glacial acetic acid. By using sodium acetate with acetic anhydride, however, excellent results were obtained. The significant conclusion was reached that unless an α -halo diketone is capable of existing in an enolic form it is not affected by acetic anhydride alone or by acetyl chloride. In the presence of potassium acetate, however, acetic anhydride greatly surpasses potassium acetate dissolved in acetic acid in acetylating power. They also noted that the effectiveness of the potassium acetate-acetic anhydride reagent seemed to be the concentration of the potassium acetate.

Clark, Cox, and Mack (6), in a study of the action of chloro-

dimethyl ether on salts of organic acids, found that chloromethyl methyl ether was easily converted to methoxymethyl acetate by refluxing the chloro ether for eight hours with fused sodium or potassium acetate. The reflux temperature was 120°C.

The reactions given above are pertinent inasmuch as they furnish an insight into the possible methods of acetylation of the dichlorides of starch, which contain both the α -halo diketone and α -halo ether groups. In an attempt to further predict the reaction characteristics of the dichloride, investigation of the literature was continued with a view toward relating electronic effects of various groups present in the dichloride with the chemical behaviour of the molecule.

Newman (7) has presented a discussion of the theory concerning the existence and stability of the carbonium ion. The possibilities of double bond formation in the ring and between carbons 5 and 6 are covered briefly in a paper contributed by this laboratory (1). Various other electronic effects of atoms and groups of atoms are extensively treated by Remick (8). The significance and applications of these effects in relation to the dichlorides of starch are treated in a later section.

METHODS

Preparation of Dichlorides

The original starch used in the chlorination process was obtained from yellow hybrid corn by milling and purification methods carried out in this laboratory. The steps of preparation included steeping, hydraulic milling, screening, settling, tabling, filter-

gassing step was employed. The sample was transferred from the glass liner to a tared 125 ml erlenmeyer flask with a standard taper ground glass neck. The flask was fitted with a standard taper joint through which an air inlet and exit were constructed in order to maintain a sweeping action of the gases evolved by the sample. The air sweep exit was connected to a bubble tube scrubber containing water. The system was maintained at approximately 10 mm pressure by a vacuum pump. A stopcock placed in the inlet tube controlled the amount of air entering the flask. Since it was known that moisture caused undesirable effects on the chlorinated starch, the inlet stopcock was kept closed during the degassing period, and opened only when it was desired to equalize pressures at the end of the degassing treatment.

It has been shown (3, 9) that during the chlorination reaction, certain structures are formed which are not stable above room temperature. Since it was necessary that these structures be preserved during degassing in order to complete a structural analysis of the sample, the flask was packed in ice. The scrub tube was also packed in ice to reduce the tendency of the water to boil away due to the low pressure of the system.

Any residual hydrogen chloride gas which was evolved by the sample during degassing was caught in the bubble tube scrubber. At the end of the 24-hour degassing period, the flask with its contents was removed from the system and carefully weighed. It was then replaced in the system, and an oil bath, which was thermostatically controlled to 70°C., was substituted for the ice pack surrounding the flask. The scrub tube was filled with 100 ml of 0.6 N so-

ing, drying, and grinding. In addition, extraction of all alcohol-soluble constituents was accomplished by refluxing the starch five times in 85 per cent methanol. The methanol was removed by repeated washing with distilled water, and the starch was thoroughly dried and pulverized. The resulting product was a starch of clean white appearance, high viscosity, and low alkali number. These properties are characteristic of a well-prepared undegraded starch.

Samples of the starch were chlorinated in accordance with the procedure developed by Barham and Thomson (2, 9). Approximately 15 g was introduced into the autoclave with 450 g of liquid chlorine, and the reaction allowed to proceed 72 hours at 70°C. Of the several samples so chlorinated, three were selected to be subjected to the structure analysis procedure and to be used in the acetylation studies. These were called products III, IV, and V.

Degassing and Pyrolysis

The number of hydrogen atoms per glucose unit which were removed from the starch in the form of hydrogen chloride was found by allowing the gases from the chlorination autoclave to bubble through a scrub tube containing water. Upon completion of the chlorination reaction, the glass liner which contained the sample was removed from the autoclave and placed under a bell jar. The bell jar was evacuated, and the adsorbed chlorine allowed to volatilize at room temperature. It was found that six to eight hours was sufficient to remove all but a small amount of chlorine so adsorbed.

In order to remove the last traces, however, a subsequent de-

dium hydroxide solution and packed in ice as before. The system was again evacuated to 10 mm pressure and allowed to pyrolyze for 36 hours. The above degassing and pyrolysis procedures are based on those developed by Barham, Thomson, and Stickley (3, 9).

Structure Analysis

An inspection of the glucose unit of starch shows that of the six carbons of the glucopyranose ring, three are similar in that they hold a hydroxyl group and either one or two hydrogens (carbons 2, 3, and 6), while the remaining three hold only a hydrogen (carbons 1, 4, and 5). The structure of the glucose unit is such that only these hydrogens and hydroxyl groups can be replaced or modified if hydrolysis of the ether linkages does not occur.

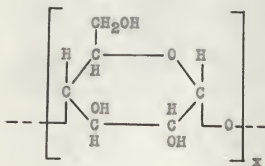


Fig. 2. The α -glucopyranose unit of starch.

During the chlorination period, it has been indicated (9) that carbons 5 and 6 remained unchanged until the reaction entered the trichloride stage. Considering carbons 1, 2, 3, and 4, it can be shown that for carbons 1 and 4 only two possible structures exist, as shown by Figs. 3 and 4. For carbons 2 and 3 five possible struc-

tures are shown by Figs. 5, 6, 7, 8, and 9.



Fig. 3. Original structure.



Fig. 4. Stable chloride.



Fig. 5. Original structure.



Fig. 6. Chlorocarbinalol.



Fig. 7. Hypochlorite.



Fig. 8. Chlorohypochlorite.



Fig. 9. Carbonyl.

All of these structures as they occur in the starch chlorides are thought to be stable below room temperature, while at 70°C. only those represented by Figs. 3, 4, 5, and 9 remain as shown. The chlorocarbinalol structure loses hydrogen chloride and becomes a carbonyl group. The hypochlorite group also loses hydrogen chloride

and becomes a carbonyl group. The chlorohypochlorite group loses chlorine in its conversion to the carbonyl structure. Thus by trapping the chlorine and hydrogen chloride evolved during pyrolysis, conclusions can be drawn concerning the extent of the chlorination reaction.

The ability of the structures of Figs. 7 and 8 to liberate iodine from potassium iodide and data obtained during the degassing and pyrolysis treatment makes possible the calculation of the exact amounts of these structures present. The data which must be obtained during the degassing and pyrolysis procedure in order to calculate the amounts of each of these structures in the glucose unit are given in the appendix. The methods of calculation are also given. These are taken from the work of Barham and Thomson (3, 9).

Acetylation

The initial investigation was designed to validate the assumption that the rapid coagulation of the starch chloride when heated in glacial acetic acid involved the replacement of a chlorine atom by an acetate group. The object was to show the per cent increase in weight of the starch dichloride caused by the replacement of the chlorine atom by the heavier acetate group.

Method 1. Twelve 50 ml beakers were carefully washed, oven dried, and placed in a desiccator which was then placed in a thermostatically controlled water bath maintained at 40°C. The desiccator was evacuated to one mm pressure and allowed to stand 12 hours. Upon removal from the desiccator, the beakers were placed in a second desiccator containing phosphorous pentoxide.

Each beaker was weighed on an analytical balance. Approximately 0.5 g samples of the starch dichloride were weighed into the beakers followed by 10 ml of the acetylating reagent. To the first six beakers was added glacial acetic acid (99.5 per cent), while for the remaining six samples acetic anhydride was used. The contents of each beaker were heated and allowed to boil 30 seconds, whereupon the beakers were placed in the 40°C. vacuum desiccator.

By maintaining the pressure at 100 mm and allowing a small stream of dried air to pass through the desiccator, the acetic acid and acetic anhydride were evaporated from the solid material in the beakers. When evaporation had proceeded to the point where bumping of the liquid due to low-pressure boiling was no longer possible, the air stream was shut off and the pressure reduced to one mm. At approximately 24-hour intervals the pressure was equalized, the beakers removed and placed in the phosphorous pentachloride desiccator for at least 30 minutes, and the weight of the beakers recorded. The beakers were then replaced in the vacuum desiccator as described above. This procedure was repeated until the beakers assumed a constant weight.

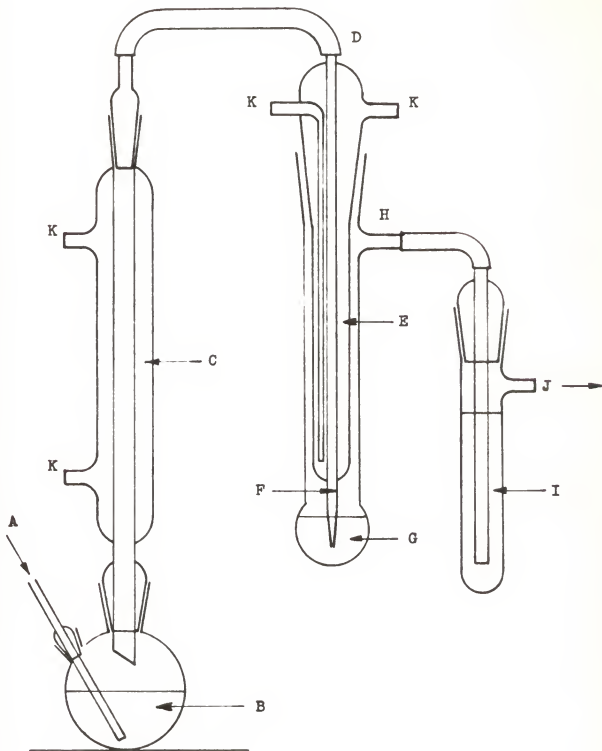
As a precaution against the presence of entrapped solvent, the samples were thoroughly broken up, pulverized, and further desiccated to constant weight. The per cent increase in weight of each sample was calculated, and the per cent chlorine of each sample determined.

In the preceding method one of the products of the acetylation reaction was isolated. The second approach to the problem was to isolate and determine quantitatively another product of the

EXPLANATION OF PLATE I

- A - Nitrogen gas inlet
- B - Acetic anhydride maintained at reflux temperature
- C - Condenser
- D - Junction of rubber tubing and sweep tube where acetic acid is added to the system
- E - Cold finger condenser
- F - Nitrogen sweep tube
- G - Reaction mixture: acetic acid and starch dichloride
- H - Nitrogen and hydrogen chloride outlet
- I - Water
- J - Nitrogen outlet
- K - Connections for cooling water inlets and outlets

PLATE I



reaction. According to the theoretical equation, for each chlorine atom that is replaced by the acetate group a molecule of hydrogen chloride is formed. Thus to determine the amount of hydrogen chloride generated during the reaction became the next objective.

Method 2. The apparatus used consisted of a reaction tube which was connected to a bubble scrub tube filled with water to absorb the hydrogen chloride formed. The sweeping of the hydrogen chloride gas from the reaction tube into the scrubber was accomplished by passing a stream of nitrogen through the system. To make the system as anhydrous as possible, the nitrogen gas was bubbled through acetic anhydride which was at its reflux temperature. The complete system is shown in Plate I.

A sample of 0.5 to 1 g was placed in the reaction tube and the nitrogen gas allowed to pass through the system at a rate of approximately a bubble a second. This sweep was maintained for a period of 12 to 16 hours before the addition of the acetic acid in order to remove any adsorbed hydrogen chloride which had formed due to slight decomposition of the product during storage.¹

In the reaction studies requiring a completely anhydrous system, precautions were taken to maintain such conditions throughout the entire run, and the acetic acid used was boiled with a small amount of acetic anhydride to remove any trace of water. At the end of the pre-sweep period, 15 ml of the acid was added through

¹Products III, IV, and V were stored in a cold room at -20°C. Decomposition at this temperature is negligible, but the necessity of exposing the products to the air during handling and sampling allowed them to come in contact with air moisture. The presence of the water so absorbed is known to bring about a reaction involving the production of hydrogen chloride.

the nitrogen sweep tube at the junction of the rubber tubing and the reaction flask, and the sweep continued. The reaction tube was immersed in a water bath controlled at 70°C. throughout the entire experiment. This temperature was chosen since the possible decomposition at higher temperatures would produce hydrogen chloride not formed by the acetylation reaction. The cold finger condenser was turned on immediately following the addition of the acetic acid.

The water in the scrub tube was removed from the system at various time intervals and replaced with fresh water. The used scrub water was made up to approximately 200 ml in a 400 ml beaker, five ml of 1:1 nitric acid added, and the chloride ion precipitated as silver chloride by 0.5 N silver nitrate. The silver chloride was filtered into a tared fritted glass crucible, dried, and weighed.

Method 3. It was also desired to investigate the extent and rapidity of acetylation of the dichloride using as the acetylating reagent sodium acetate dissolved in acetic anhydride. The sodium acetate used contained three molecules of water of hydration, therefore the solution was boiled a few minutes to bring about the reaction of any free water with the acetic anhydride. It was assumed that any unreacted water remaining after such treatment would not be capable of interacting with the starch chloride.

Approximately 0.5 g samples were placed in glass-stoppered containers of about 75 ml capacity originally designed as centrifuge tubes, and 15 ml of a solution consisting of 6.8 g of sodium acetate dissolved in 100 ml of acetic anhydride was added. The

tubes were then placed in a 70°C. water bath and allowed to stand. After a 26-hour period, the tubes were removed from the bath, cooled to room temperature, and the precipitated sodium chloride filtered into tared fritted glass crucibles. The crucibles were dried and weighed. It was noted that a certain amount of impurities was present as evidenced by the light brown color of the sodium chloride; therefore the precipitate was washed through the crucible and into a 400 ml beaker with hot water. The chloride ion was then precipitated as silver chloride. The silver chloride was filtered into a tared fritted glass crucible, dried, and weighed. From the amount of chloride obtained by this method the number of chlorine atoms per glucose unit replaced by the acetate group during the 26-hour period was calculated.

RESULTS AND DISCUSSION

Structure Analysis

The three samples of starch dichloride selected for the acetylation studies were designated as products III, IV, and V. From the degassing and pyrolysis data obtained during their preparation, the amounts of the various structures present in their glucose units were determined by the method of calculation given in the appendix. These values are given in Table 1.

Products III and IV have progressed slightly into the trichloride stage as shown by the values of 2.15 and 2.22 for their stable chloride. As it has been shown (9), the first two carbon-bound (stable) chlorine atoms occupy carbons 1 and 4, and the third chlorine must then assume its position on carbon 5. The value of less

than one for the hydroxyl structure is explained on the basis of a partial oxidation of the hydroxyl remaining on carbon 6 through the formation of the intermediate hypochlorite or chlorocarbino1 structure which is subsequently converted to the carbonyl structure by pyrolysis. It is of interest to note that a small amount of residual oxidizing power remains in these samples after prolonged pyrolysis. It indicates a hypochlorite structure of 0.02 in product III. The molecular weight per glucose unit of products III, IV, and V as found by combining the amounts of each structure present is 231, 233, and 225 respectively. A second method of calculation of the molecular weights by noting the weight changes of the products during the chlorination, degassing, and pyrolysis gave 231, 232, and 226 respectively.

Table 1. Structure analysis of the pyrolyzed products III, IV, and V.

Structure per glucose unit	Product III	Product IV	Product V
Carbonyl	2.13	2.47	2.29
Hydroxyl	0.86	0.53	0.70
Chlorohypochlorite	0.00	0.00	0.00
Hypochlorite	0.02	0.00	0.00
Chlorocarbino1	0.00	0.00	0.00
Stable chloride	2.15	2.22	1.99

Acetylation

In the attempt to bring about the rapid coagulation of the dichlorides (products III, IV, and V) by heating them in glacial acetic acid, it was found that all three products were completely soluble in the acetic acid even at room temperature. The resulting yellow-green solution darkened rapidly when heated to boiling, but

no solid phase was detected. Duplicate samples of each of the three products were treated with glacial acetic acid and acetic anhydride (Method 1). The resulting data are recorded in the following tables.

Table 2. Glacial acetic acid and starch dichloride: 30-second reflux followed by desiccation.

Analysis data				Chlorine atoms replaced per glucose unit	
Product	Weight of sample	% increase in wt.	% Cl of residue	Calculated from % wt. increase	Calculated from % Cl of residue
III	0.5830	3.93	27.17	0.38	0.33
III	0.5341	4.49	27.28	0.44	0.31
IV	0.5070	1.02	26.42	0.10	0.47
IV	0.6143	3.60	26.13	0.35	0.45
V	0.4378	4.00	24.33	0.38	0.38
V	0.5170	4.12	24.62	0.40	0.36

The number of chlorine atoms replaced per glucose unit was calculated by two methods, as shown in the last two columns, Table 2. Since the replacement of a chlorine atom by an acetate group results in an increase in the molecular weight of the glucose unit, the increase in weight of the sample after the acid treatment becomes a means of measuring the extent of the reaction. Similarly, the decrease in the per cent chlorine of the sample, which is due to both the loss of chlorine and the increasing sample weight, is used as a second method of calculation of chlorines replaced. These values are seen to be in fair agreement, the average values for the two methods being 0.34 and 0.38 respectively.

Table 3. Acetic anhydride and starch dichloride: 30-second reflux followed by desiccation.

Analysis data				Chlorine atoms replaced per glucose unit	
Product	Weight of sample	% increase in wt.	% Cl of residue	Calculated from % wt. increase	Calculated from % Cl of residue
III	0.5038	12.98	26.27	1.27	0.23
III	0.4229	12.60	25.99	1.23	0.26
IV	0.7024	14.55	25.51	1.43	0.27
IV	0.6885	14.35	26.03	1.41	0.28
V	0.6316	14.44	23.78	1.38	0.26
V	0.4435	14.56	23.82	1.40	0.26

In comparing the last two columns of Table 3, it was found that the calculation of chlorines replaced on the basis of per cent increase in weight of the sample did not agree with that based on the per cent chlorine in the residue. This discrepancy can be explained only by assuming an increase in weight of the sample due to some other effect or reaction not involving the replacement of a chlorine atom. There are two possibilities to be considered. First, the adsorption of unreacted solvent which could not be removed under the imposed conditions would give such an effect; and second, the reaction of the acetic anhydride with some functional group in the glucose unit other than the chlorine would also account for this phenomenon.

Considering the fact that samples differing widely in their original weights gave values for their per cent increase in weight which were in close agreement, the possibility of adsorption of the acetic anhydride is improbable. It is quite possible, however, that the acetic anhydride could react with the hydroxyl group on carbon 6, Fig. 1, resulting in acetylation of carbon 6 and the for-

mation of a molecule of acetic acid. In support of this theory it should be noted that interaction of the chlorine atom and the acetic anhydride is unlikely to result in acetylation, since the formation of acetyl chloride would be necessary as a product of the reaction.

If it is assumed that acetylation of carbon 6 first occurs, the resulting acetic acid molecule could then replace the chlorine atom on carbon 1 resulting in the production of hydrogen chloride. The lower values of the number of chlorines replaced by acetic anhydride supports this theory. On the basis of this mechanism it was calculated that 66 per cent of the hydroxyl groups on carbon 6 were replaced by the acetate group.

It was evident that the early investigations of the coagulation phenomenon of starch dichlorides in acetic acid could not be compared with the results obtained above. The differences in behavior of the products prepared for this investigation and those used in the earlier experiments cannot be explained without speculation. The physical state of the granules (9) conceivably could cause varying degrees of reactivity and solubility, while the possibility of a monochloride appearing as a dichloride due to the presence of large amounts of the unstable hypochlorites and chlorocarbonols must not be overlooked.

When it became evident that the 30-second reflux period resulted in the replacement of less than 0.4 chlorine atoms per glucose unit, the second method was devised to gain a knowledge of the speed and extent of the reaction. Samples of each of the three products were treated according to the procedure of Method

2, and the resulting data were plotted, Fig. 10. Zero time represents the time of addition of the acetic acid. The value of the ordinate at zero time indicates the equivalents of chlorine per glucose unit which have formed hydrogen chloride by decomposition.

The acetylating reagent for each of these curves was 15 to 25 ml of a solution prepared by boiling together 150 ml of 99.5 per cent acetic acid and six ml of 99 per cent acetic anhydride. The amount of reagent added was determined by the weight of the dichloride sample, which varied from 0.5 to 1 g. In each run the acetic anhydride scrub was employed to guard against the presence of moisture in the nitrogen sweep gas.

Each of the three curves, Fig. 10, is characterized by a rapid production of hydrogen chloride in the initial stage of the reaction. This is followed by a gradual decrease until a constant rate is approached. The extent and rate of the initial reaction stage is seen to vary with the different products. Attempts to determine the order of the reaction by plotting time-concentration curves for the hydrogen chloride were fruitless; however, the possibilities of simultaneous reactions, consecutive reactions, and steric effects make such a kinetic analysis unwarranted.

To show the effects of various changes of system conditions on the rate of reaction, the four curves, Fig. 11, are given. The portions of the curves shown by dotted lines are not supported by actual data but represent the most probable values. Runs C-41, 42, and 46, Fig. 11, were carried out in the anhydrous system as described in Method 2. Run C-40 was a duplicate of C-41 with the ex-

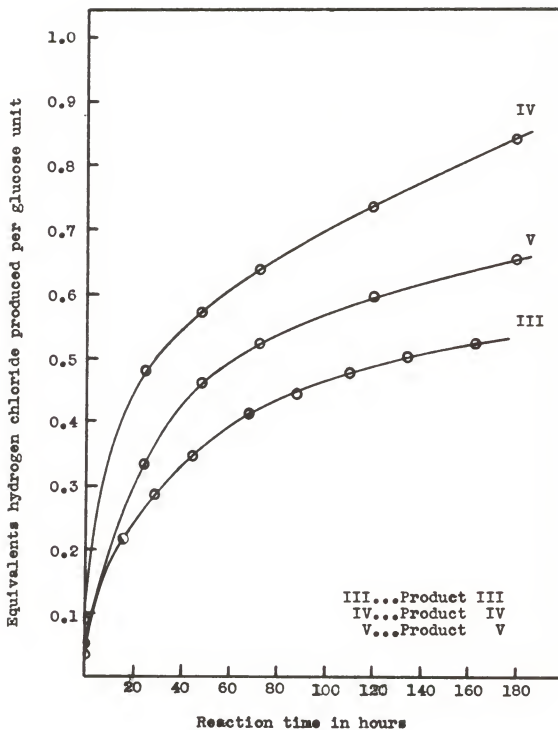


Fig. 10. The rate of hydrogen chloride production. Starch dichloride in glacial acetic acid.

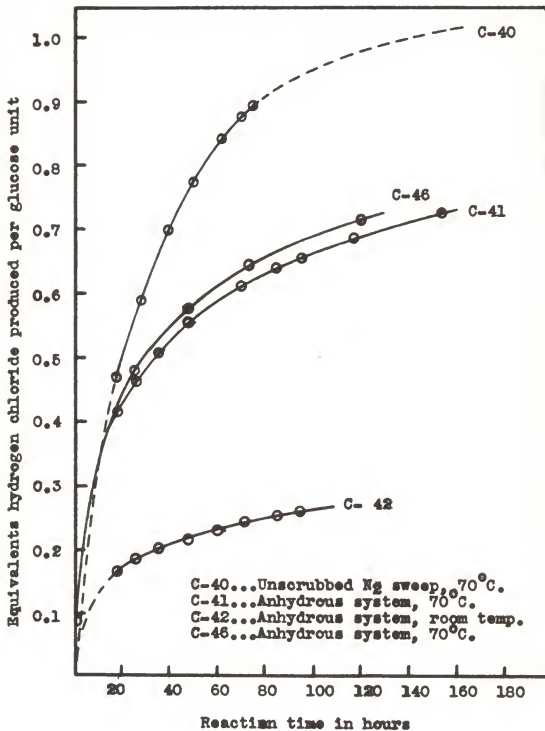


Fig. 11. The rate of hydrogen chloride production under various conditions. Product IV.

ception that the nitrogen sweep gas was used directly from the tank (no acetic anhydride scrub was employed). Run C-42 was executed under anhydrous conditions at room temperature. For C-40, C-41, and C-42 no initial flushing of the dry sample before addition of the acid was made; while C-46 represents a run similar to C-41, but in which the adsorbed hydrogen chloride in the dry sample was determined before the reaction was initiated. The dichloride used for all of the reactions indicated in Fig. 11 was product IV.

A comparison of C-41 and C-42 indicates that the rate of the production of hydrogen chloride varies with the temperature, however, considering the 30 to 40 degree difference in the temperatures at which these runs were made, the temperature coefficient of the rate is abnormally low for an organic reaction.

The rapid rate and extent of curve C-40 is thought to be due to the continuous addition of moisture to the system by the nitrogen sweep gas. The exact function of moisture in the system is not known; however, it is noted that increased hydrogen chloride production results, as shown by a comparison of C-40 and C-41. Whether water would react with the dichloride or assume the role of a catalyst cannot be decided without further investigation; although evidence indicates that both could be possible.

The replacement of the chlorine atoms by acetate groups was thus shown to be a very slow reaction when acetic acid was used as the reagent. In an attempt to bring about a faster and more complete reaction, attention was turned to the use of the salts of

acetic acid.

Since it was shown by Barnes and Tulane (4) that one of the most powerful acetylating reagents is sodium acetate dissolved in acetic anhydride, such a reagent was prepared and duplicate samples of products III, IV, and V were treated as given in Method 3. The results obtained are listed in Table 4.

Table 4. Acetylation of starch dichloride with sodium acetate in acetic anhydride.

Sample data		Chlorines replaced per glucose unit	
Product	Wt. of sample	Calc. from wt. NaCl	Calc. from wt. AgCl
III	0.5823	1.08	-
III	0.6124	1.14	-
IV	0.8334	1.40	1.39
IV	0.4072	1.32	1.36
V	0.5616	1.17	1.18
V	0.5092	1.17	1.17

The calculation of chlorines replaced per glucose unit was corrected for the amount of sodium chloride soluble in the acetic anhydride although the experimental value obtained can be only approximate. A saturated solution of the acetic anhydride reagent as prepared (Method 3) and sodium chloride (room temperature) was found to contain 0.0004 mg of sodium chloride per ml. This value is assumed to be the maximum since the presence of dissolved starch dichloride would tend to decrease the solubility of the salt; however, it is possible that increased solubility would result.

Although the samples were allowed a 26-hour reaction period, it is doubtful that such a length of time was required for comple-

tion of the reaction. It was noted in a preliminary experiment that even at room temperature the darkening of the solution (which appeared a deep blood red color by transmitted light) and the apparent amount of sodium chloride precipitated did not increase appreciably after six hours.

In all cases the chlorines replaced per glucose unit (columns 3 and 4, Table 4) exceeded the value of one. The missing values (column 4) are the result of faulty laboratory technique; however, the corresponding values of column 3 are close approximations to those lost.

In comparing the chlorines replaced per glucose unit by Methods 1, 2, and 3, a relationship was found to exist between the extent of chlorination of the product and its ease of acetylation. These comparisons are summarized in Table 5. Values for each of the methods are the mean values of the duplicate runs.

Table 5. A comparison of the extent of chlorination with ease of acetylation.

Pyrolyzed product data					Chlorines replaced per glucose unit		
Product	Cl	OH	O	%	Method 1	Method 2	Method 3
	C_G	C_G	C_G	Cl			
	:	:	:	:			
IV	2.22	0.53	2.47	33.98	0.46	0.57	1.38
V	1.99	0.70	2.29	31.30	0.37	0.46	1.17
III	2.15	0.86	2.13	33.20	0.32	0.36	1.11

The products are listed in order of decreasing ease of acetylation. It is significant that the per cent Cl of the products as well as the carbon-bound Cl_G^* (Table 5) does not follow this order. Thus the extent of oxidation of the glucose unit by the

*The subscript "G" signifies "per glucose unit".

chlorine as it progresses into the trichloride stage seems to be the rate factor involved. Whether this be a steric effect or the activation of the chlorine due to the formation of an activating functional group through oxidation is a matter of conjecture.

Although the data obtained in the various methods are not sufficient to establish the complete mechanism of the acetylation of the starch dichlorides, several indications of the nature of the reaction mechanism are found to exist. These observations and their interpretations are listed below.

1. The speed and extent of acetylation was greatly increased by the addition of sodium acetate. This strongly indicates the theory that the acetate ion concentration is the rate-controlling factor. This view is in accordance with the observations of Barnes and Tulane (4), and it is also significant that all other acetylation methods of similar compounds found in the literature made use of sodium or potassium acetate. Since glacial acetic acid is known to be only slightly ionized, the slow reactions obtained with that reagent can be explained by the relatively low concentration of acetate ions. It is possible that water could exert a catalytic effect since its presence in the system would produce greater ionization of the acetic acid giving hydronium ions and an increased concentration of acetate ions. It is known that water reacts with the starch dichloride, but whether it would be able to do so in the form of a hydronium ion must be considered. If the water not involved in hydronium ion formation reacted with the starch dichloride, replacing the chlorine with a hydroxyl group, the removal of the hydrogen chloride so formed

would shift the equilibrium of the acid ionization reaction so that eventually all water would be removed from the system.

Further data must be obtained before the role of water in the reaction can be ascertained. It is interesting to note, however, that any hydroxyl groups formed through reaction with water would, in all probability, be replaced by the acetate group through the action of the acetic anhydride.

2. One of the stable carbon-bound chlorines is evidently not replaceable by the acetate group under the conditions imposed. Since inspection of the glucose unit of the dichloride shows that one of the chlorines (carbon 1) is attached to a carbon which is involved in an acetal structure, it is assumed that the relative electron density of that carbon would be enhanced. The chlorine atom would thus be held less tightly, allowing a greater ease of replacement. Whether the chlorine atom actually exists as a chloride ion in the acetic acid solution is not known. Such an ionization would lead to the formation of a carbonium ion, which is discussed by Newman (7). According to his theory, the carbonium ion may exist only momentarily, or may become a structure of long life through resonance stabilization. Since double bond formation in the pyranose ring has been shown to be improbable by studies of actual scale models of the glucose units (1), stabilization by resonance is doubtful.

3. As was shown by Barnes and Tulane (4), the removal of an α -halo atom of a diketone is easily accomplished by sodium acetate dissolved in acetic anhydride. Experimental evidence indicates, however, that one of the chlorines of the dichloride is not

susceptible to such a reagent. A chlorine atom on carbon 4 or 5, while not as loosely held as the chlorine on carbon 1, would still be influenced by the adjacent ether linkage and should be easily replaced according to electronic theory. These observations indicate the presence of a steric effect which prohibits the approach of the reactant molecule. As shown by Table 5, the partial destruction of the structure surrounding carbon 6 results in an increased rate and extent of acetylation.

SUMMARY

1. The existence of a reaction between the dichloride of starch and glacial acetic acid was established. Calculations from data obtained indicated a reaction involving the replacement of a chlorine atom by an acetate group. Similar data obtained using acetic anhydride as the acetylating reagent gave evidence of a reaction involving the replacement of the hydroxyl group on carbon 6 by an acetate group.

2. The rate of acetylation of the dichlorides at 70°C. and at room temperature was determined using as the acetylating agent glacial acetic acid in an anhydrous system. The rate was found to decrease with time, but an attempt to determine the order of the reaction was unsuccessful. An increase in the rate of hydrogen chloride production was noted when traces of moisture were allowed in the system.

3. The use of sodium acetate in acetic anhydride as the acetylating reagent resulted in a rapid reaction which terminated with the replacement of slightly more than one chlorine per glucose

unit. A correlation between the extent of chlorination and the extent of acetylation of the chlorinated products was noted.

4. The comparison of results obtained from the several methods of study of the reaction gave evidence of the existence of steric hindrance of such a nature as to inhibit the replacement of one of the chlorines. The electronic effects relative to the availability of the chlorines were also discussed.

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APPENDIX

The following outline is a summary of the experimental procedures and calculations involved in the determination of the structure of the chlorides of starch. The material given is a condensed form of the procedures developed by Barham, Thomson, and Stickley (2, 3, 9).

A. Chlorination

1. Weight of starch used

a. Calculation:

as recorded.

2. Equiv. starch used (glucose unit)

a. Calculation:

$$\text{Equiv. glucose units} = \frac{A1^*}{162.16}$$

3. H_G lost during chlorination

a. Experimental:

The scrub solution through which the bomb gases are passed is made up to 1000 ml and 25 ml aliquots are taken for a triplicate analysis. The dissolved chlorine is boiled out and the solution made acidic with 5 ml of 1:1 nitric acid. After filtration the chloride is precipitated with 0.5 N silver nitrate. After digesting the precipitate on the hot plate in the dark until well coagulated, it is allowed to stand (in the dark) for at least three hours before filtering into a tared fritted glass crucible.

b. Calculation:

$$H_G = \frac{40 \times \text{wt. AgCl ppt.}}{A2 \times 143.34}$$

*Refers to the value of section A, subdivision 1 of this outline.

B. Degassing1. H_G lost during degassing

a. Experimental:

The scrub water is made up to 500 ml and three 100 ml aliquots taken. The dissolved chlorine is boiled out and the chloride precipitated as above (A.3.a.).

b. Calculation:

$$H_G = \frac{5 \times \text{wt. AgCl ppt.}}{A2 \times 143.34}$$

2. Weight of product after degassing (actual)

a. Calculation:

as recorded.

3. Per cent chlorine of degassed product

a. Experimental:

After product is thoroughly mixed in the flask, 0.2 to 0.3 g samples are weighed into the Parr bomb cups. Following the sample in the cup are 0.7 g of powdered sucrose, 0.5 g of powdered potassium nitrate and a measuring dipper of sodium peroxide (the Parr instruction booklet should be consulted before using bombs). The bombs are closed, well shaken, and fired. When cool, the bombs are disassembled, the lids carefully lifted, and the lids thoroughly washed with a fine stream of hot water. The water is caught in a 400 ml beaker until the water level in the beaker is about 0.5 inches. The cup is then placed in the beaker and rolled back and forth to allow its contents to dissolve in the water. When the reaction has subsided and solution is complete, the cup is removed and washed with hot water, catching the water in the beaker. To the solution in the beaker is added 55 ml of 1:1 nitric acid in small portions while stirring vigorously. The solution is boiled until clear and filtered through a Whatman No. 2 filter into a 600 ml beaker. The chloride is then precipitated and weighed as above (A.3.a.).

b. Calculation:

$$\% \text{ Chlorine} = \frac{24.738 \times \text{wt. ppt.}}{\text{wt. sample}}$$

4. Calculated weight of product

a. Calculation:

$$\begin{array}{l} \text{Theoretical weight} \\ \text{of chlorinated,} \\ \text{degassed sample} \end{array} = \frac{A2 \times (162.16 - (A3 + B1)(1.008))}{1 - B3}$$

5. Molecular weight of degassed product

a. Calculation:

$$\text{M.W.}_G = \frac{B4}{A2}$$

6. OCl_G of degassed product

a. Experimental:

Three iodometric flasks are prepared containing 30 ml each of the following solution:

10 ml 30% KI
10 ml 0.1 N HCl
10 ml H_2O

Samples of 0.2 to 0.4 g are weighed in an aluminum weighing dish and transferred to the flask. The flasks are swirled and allowed to stand 15 to 20 minutes, and they are titrated with 0.1 N sodium thiosulfate to a starch indicator endpoint.

b. Calculation:

$$\text{OCl}_G = \frac{(\text{ml thiosulfate} \times N) \times B5}{2000}$$

C. Pyrolysis

1. Weight of product before pyrolysis

a. Calculation:

as recorded.

2. Equiv. glucose units in product

a. Calculation:

$$\text{Equiv.} = \frac{C1}{B5}$$

3. Weight of product after pyrolysis

a. Calculation:

as recorded.

4. Molecular weight per glucose unit of pyrolyzed product

a. Calculation:

$$\text{M.W.}_G = \frac{C3}{C2}$$

5. Per cent chlorine of pyrolyzed product

a. Experimental:

see B.3.a.

b. Calculation:

see B.3.b.

6. OCl_G of pyrolyzed product

a. Experimental:

see B.6.a.

b. Calculation:

see B.6.b.

7. Cl_{2G} lost during pyrolysis

a. Experimental:

Iodometric flasks are prepared as in B.6.a. and 50 ml portions of the scrub (which is made up to 500 ml) are added to the flasks followed immediately by five ml 1:1 sulfuric acid. After 15 to 20 minutes, titration is carried out as in B.6.a.

b. Calculation:

$$\text{Cl}_{2G} \text{ lost} = \frac{\text{ml thiosulfate} \times N \times C4}{2000 \times \text{wt. sample}}$$

8. HCl_G lost during pyrolysis

a. Experimental:

Triplicate 50 ml portions of the 500 ml scrub solution are pipetted into iodometric flasks and a few boiling chips added. Enough crystalline potassium iodide is added to reduce all OCl to chloride ion. One equiv. of OCl requires two equiv. of potassium iodide. The number of equiv. of OCl per 500 ml is calculated and divided by 5 to give equiv. of potassium iodide needed, and a slight excess is added. The solution is made acidic with 5 ml of 1:1 sulfuric acid and all free iodine boiled out. When the solution is clear, a little potassium nitrite is added to destroy the excess potassium iodide, and the solution is again boiled until clear. Potassium nitrite may be added in small increments to test for completeness of potassium iodide destruction. The solution is filtered, five ml 1:1 nitric acid is added, and the chloride ion precipitated as in A.3.a.

b. Calculation:

$$\text{HCl}_G \text{ lost} = \frac{(10 \times \text{wt. ppt.})}{2} - 2(C7)$$

D. Structure analysis calculations (after pyrolysis)1. Carbonyl $_G$

$$= \frac{(A3 + B1 + C8) - D6}{2}$$

2. Hydroxyl $_G$

$$= 3 - (D1 + C6)$$

3. Chlorohypochlorite $_G$

$$= \text{zero}$$

4. Hypochlorite $_G$

$$= C6$$

5. Chlorocarbino $_G$

$$= \text{zero}$$

6. Stable chloride_G

$$= \frac{(C5 \times C3)}{35.46 \times C2} - C6$$

7. M.W._G (from D.1.,2.,3.,4.,5.,6.)

$$= D1(16.00) + D2(18.02) + D4(52.47) \\ + D6(35.46) + (3 - D6)(1.01) + 104.06$$

E. Structure analysis calculation (before pyrolysis)

1. Carbonyl_G

$$= \frac{(A3 + B1) - E5 - E3}{2}$$

2. Hydroxyl_G

$$= 3 - (E1 + E3 + E6)$$

3. Chlorohypochlorite_G

$$= C7$$

4. Chlorocarbonol_G

$$= C8 - E6$$

5. Stable chloride_G

$$= \frac{B3 \times B4}{35.46 \times A2} - 2(E3) - E6 - E4$$

6. Hypochlorite_G

$$= B6 - C7$$

7. M.W._G (from E.1.,2.,3.,4.,5.,6.)

$$= E1(16.00) + (E2 - E4)(18.02) + \\ E4(52.47) + E5(35.46) + E6(52.47) \\ + 104.06$$

Date Due

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