A STUDY OF THE HYDROLYTIC AND OXIDATIVE DEGRADATION
OF SOME CHLORINE DERIVATIVES OF STARCH

by

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INTRODUCTION

Today starch is one of the most important raw materials available to mankind. Its uses are many and varied. With the aid of scientific progress, the importance and the uses of starch undoubtedly will multiply many more times in the future.

The use of starch appears to date back as far as 3500 B. C. Small amounts of a starch adhesive have been found on Egyptian documents of this approximate date (9). From cereal grains, the preparation of starch has been described by Marcus Procius Cato as far back as 184 B. C. The method of extracting starch from grain appears to have been discovered by the inhabitants of the Isle of Chios. The manufacture of starch from wheat became an important industry in Holland in the middle ages. At this time starch was considered a luxury and was used by the dignitaries for stiffening fabrics. From the sixteenth century to the eighteenth century starch was used in the custom of powdering hair (6).

As the demand for starch grew, it was manufactured more and more on an industrial scale. However, it is interesting to note that at one time in England the manufacture of starch was prohibited by the State because it involved the diversion of wheat from its more legitimate use as a food (9). With the growth of the demand for starch came competition, better means of manufacture, and modification into many more useful products. The manufacture of starch and its modification became an art of great importance. Today much of the starch industry is still based on "the art"; however the gap between science and this art is rapidly closing.

The structure of starch has engaged the attention of many workers, and the investigation of this problem is still proceeding vigorously. In the past three decades, great advances have been made towards its solution, although in the present state of our knowledge it is sometimes difficult to reconcile the various views concerning the nature of starch that have been put forward.

The heterogeneous nature of starch, the fact that most methods of attack on the problem of its structure are those involving degradation of the molecule, and consideration of the source and pretreatment has rendered investigation difficult. Some investigations have involved the preparation of derivatives of starch and subsequent hydrolysis to the smaller identifiable chemical entities. Irvine (7) applied such a method in his studies of the nature of starch by exaustively methylating it and then hydrolysing this methyl derivative.

Direct chlorination of starch, which was first carried out successfully in this laboratory (1), has been repeatedly studied. Starch derivatives, in which one, two, three, and four atoms of chlorine have been introduced per glucose unit, have been prepared. The postulated structures are shown in Fig. 1. These studies of the direct chlorination of starch appear to justify certain conclusions as to the gross structure of the starch granule and indicates many possibilities for future study. The hydrolytic degradation of some of the chlorinated products is one of these possibilities.
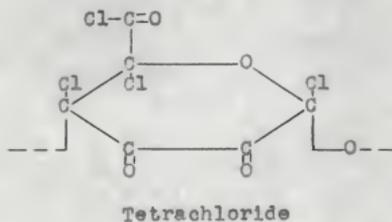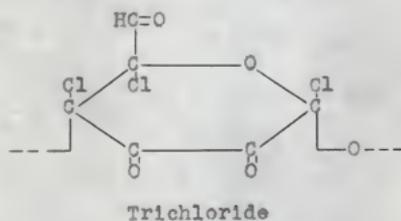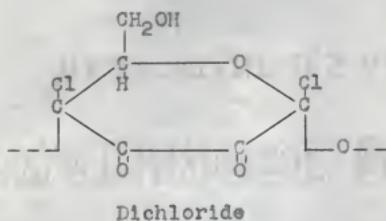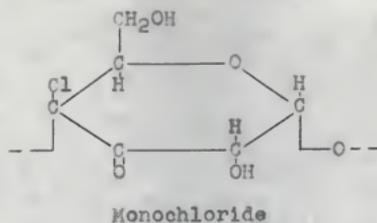
Fig. 1. Postulated repeating unit of various chlorinated
starches (11).

REVIEW OF LITERATURE

There is no record in the literature of the preparation
of the chlorides of starch except that which has been contrib-
uted by this laboratory. In 1946, Barham, Stickley, and
Caldwell (1) reported the successful chlorination of starch
with phosphorus pentachloride, and in 1950 the direct chlori-
nation of starch with liquid chlorine as carried out by Barham
and Thomson was published (2).

Valuable sources of information concerning the properties
of the chlorinated starches are the doctoral thesis submitted
by Thomson (11) and a published technical bulletin by Barham
and Thomson (2).

Thomson (11) indicated that chlorine atoms on carbon atoms
1 and 4 of the dichloride differed considerably in their sta-
bility. Bryske (3) reported that one of the chlorine atoms
of the dichloride was not removed by saponification with sodium
hydroxide in the cold. As further supplementary evidence,
Cook (5) reported that in acetylation reactions one chlorine
was replaced by the acetate group and the other chlorine atom
was unreactive to acetylation presumably because of steric
considerations.

In the course of preliminary studies of the properties
of the chlorinated starches, Thomson (11) reacted ortho
phenylene diamine with the dichloride of starch and obtained
in one instance 74 percent conversion to the α-dichlorodiketone.
This is considered a very specific test for the presence of
α-diketones.

Barham and Thomson (2) found that the chlorination of a
25 percent water starch paste gave 0.365 mole of oxalic acid;
from this it was indicated that the α-diketone structure was
present on about every third glucose ring. They also reasoned
that the formation of oxalic acid required the rupture of a
carbon to carbon bond in the glucopyranose ring, and that the
bond most likely to rupture would be the one connecting the
two adjacent carbonyl groups comprising the α-diketone structure.

Specific attempts to degrade the chlorides of starch by
hydrolysis, oxidation, or both, have not been reported
previously. This thesis is devoted to such a study.

METHODS AND MATERIALS

The chlorinated starch derivatives used were made in this
laboratory by Gerald Foster* in the course of a study of the
liquid phase chlorination of starch to the trichloride stage.
These products contained varying amounts of chlorine bound to
carbon, carbonyl groups, and carbon bound hydrogen. The
various amounts of these structures were determined by Gerald
Foster in the course of his studies of the chlorination of
starch. None of the products used in this work had progressed
completely to the dichloride stage but had approached that
stage.

Preliminary studies of several different chlorinated
starches and oxidizing agents indicated that nitric acid
offered the most promise for the degradation and subsequent

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*Graduate student in this laboratory.

identification of the degradation products. Clark (4) reported
that by the action of nitric acid starch dichloride was completely
converted to oxalic acid. In the course of the studies conducted
by the author complete conversion to oxalic acid could not be
attained. However, oxalic acid was a product of the degrada-
tion, but to a much lesser extent. By qualitative methods it
was found that besides oxalic acid, carbon dioxide, ionizable
chlorine and bound soluble chlorine were present. There was
also present small amounts of difficultly crystalizable uni-
dentified substances.

In each case degradation of the chlorinated starch was
not complete. A solid residue always resisted degradation.
This residue in every case had a chlorine content much higher
than the original chlorinated starch and was bright yellow
colored in most instances. When viewed under a microscope it
appeared to still have an organized structure typical of the
dichloride of starch. Its solubility properties were much the
same as the chlorinated starch from whence it came. It was
soluble in such solvents as ethyl alcohol, acetone, five percent
sodium hydroxide, and methyl alcohol; however it was insoluble
in the non polar solvents such as diethyl ether, carbon tetra-
chloride, and petroleum ether, and insoluble in water and five
percent acid solutions.

Since oxalic acid and carbon dioxide were the only carbon
containing products of the degradation found, and since the
carbon balance based on the respective amounts of carbon dioxide
and oxalic acid found was not commensurate with the amount ex-

pected per glucose unit, it was reasoned that other carbon
containing compounds were present but were difficult to separate
and identify. If one assumes that the oxalic acid came from the
cleaving of the alpha diketone groups, and subsequent hydrolysis
of the ether link holding the repeating units together, and that
the carbon dioxide came from decarboxylation of some of the
oxalic acid formed, it could be reasoned that four carbons of
the affected glucose units were unaccounted for. The possibili-
ties of these four carbon compounds seem most likely if one
considers a four carbon di- or mono-carboxylic acid. This acid
would be poly functional and would be difficult to separate and
identify. It is apparent also that this four carbon acid could
be a source for the carbon dioxide found and thus would lead to
still more di- and mono-carboxylic acid possibilities. Since
ordinary qualitative methods of separation of this possible
mixture were to no avail, a method of chromatagraphic separation
was used. The method of Stark, Goodban, and Owens (10) was used
since it would effect the separation of nearly all of the theo-
retically possible two, three, and four carbon non-volatile di-
and mono-carboxylic acids. Two of the several solvent mixtures
used by Stark et al, were used in developing the chromatograms.
The solvents used were solvents "F" and "D" as designated by
these authors.

In each case the only acid to appear on the chromatogram
was oxalic acid. Repeated efforts in which the conditions were
altered yielded only oxalic acid. From these results it would
appear that of possible non volatile acids, only oxalic acid

was present, or that if other non volatile acids were present,
they were present only in amounts too small to be found by
this method.

If any of the volatile acids were present, an ether extrac-
tion of the mother liquor and subsequent determination of the
Du Claux value would identify them. Attempts were made to obtain
identifiable substances in this manner both by ordinary extrac-
tion methods and by the method of continuous extraction. The
ether extract upon evaporation at room temperature yielded
nothing except a trace of non volatile liquid most of which
appeared to be water.

Preliminary experiments showed that when the mother liquor
of the reaction of nitric acid on the chlorinated starches was
evaporated, syrups or other difficultly crystalizable substances
were quite frequently evident but all efforts to isolate or
identify such products proved fruitless. Later experiments
indicated strongly that these difficultly crystalizable products
contained chlorine bound to carbon.

The qualitative experiments of the action of nitric acid
on the various chlorinated starches, and the results of previous
workers in the study of these products, led to a kinetic study.
The kinetics of a reaction may be followed in several ways.
Two of these ways were seriously considered. One was to follow
the formation of products with time, and the other was to
follow the decomposition of the chlorinated starch with time.
The latter method did not show much promise because of the
apparent complications of either a change in the original

product or of the non-homogeneous character of the product.
The former method, although not without complexity, was chosen
as the best because the change in concentration of several
reaction products could be followed with time.

In order to have sufficient quantity of the chlorinated
starch to complete a kinetic study, five of these products were
weighed very carefully and mixed together and an average of the
different structural contributions as calculated by Barham and
Thomson (2) and Thomson (11) was made by mathematical calcula-
tions. The method of these calculations was straight forward
and will not be included here. The amount of contribution of
the mixture are shown in Table 1.

Table 1. The different structural contributions of the
different chlorinated starches and the average
contribution of the mixture, designated GF-M.

Name of sample	Weight in grams	Mole weight	Chlorine percent	Moles carbonyl	HCl per glucose unit	Chlorine per glucose unit
GF-39	12.214	215.57	27.01	1.537	4.75	1.64
GF-28	13.672	210.72	25.29	1.588	4.68	1.50
GF-19	16.367	218.03	27.78	1.465	4.64	1.71
GF-15	13.154	228.49	31.16	1.372	4.75	2.00
GF-11	14.839	209.13	24.69	1.585	4.62	1.45
GF-M	----	216.26	27.14	1.510	4.68	1.65

Two grams of the mixture of chlorinated starches were
reacted with a large excess of nitric acid for varying lengths
of time. The temperature of these reactions was held constant

at 70° C. ($\pm$ .5°) by suspending the reaction vessel in an oil
bath which was thermostatically controlled. The reaction
apparatus used was a 100 ml round bottom flask with an all
glass stirrer. A reservoir for the nitric acid was attached
to the flask by means of a ground glass connection. This also
served as an inlet for nitrogen gas with which the system was
continuously swept. A scrubber was attached to a ground glass
outlet coming from the stirrer part. All connections through-
out the apparatus were made by means of ground glass standard
taper joints. The complete apparatus is shown in Plate I.

Two grams of GP-M were transferred to the reaction flask,
the side arm connection was stoppered, the stirring attachment
was put into place, and its side arm connection also stoppered.
This part of the apparatus was then lowered into the oil bath
and clamped into position with only the neck of the flask above
the liquid level of the oil bath. The scrubber section of the
apparatus then was connected to the side arm of the stirrer
part, and the stopcock in the line leading to it was opened.
Next the nitric acid reservoir was connected to the side arm
of the reaction flask and the stopcock in this line closed.
The reservoir was then filled with 80 ml of 1:1 nitric acid,
the nitrogen attachment put into place, and the nitrogen source
turned on just enough to create a slight pressure differential
above the nitric acid. All joints were checked and sealed,
the time was noted, the stirrer turned on, and the reservoir
stopcock turned to the open position. This time was recorded

EXPLANATION OF PLATE I

A - Nitrogen gas inlet

B - Nitric acid reservoir

C - Reaction flask: chlorinated starch and 1:1 nitric acid

D - Thermostatically controlled oil bath

E - All glass stirrer

F - Sodium hydroxide scrub trap

G - Nitrogen gas outlet

PLATE I
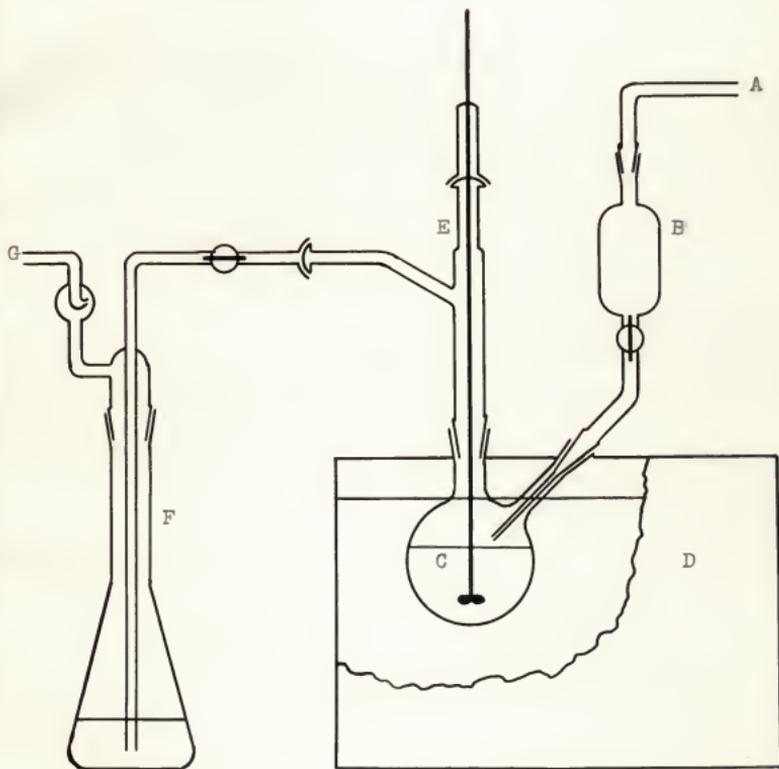
as the "zero-time". After all the nitric acid had flowed into the reaction vessel the reservoir stopcock was used to regulate the flow of nitrogen to a rate of about two or three bubbles per second through the scrubber.

In stopping the reaction, the reservoir and scrubber stopcocks were closed. This time was noted and recorded as the stopping time of the reaction. The reaction vessel was immediately removed from the oil bath and cooled to about 15° C. in a small water bath. After cooling the contents of the reaction flask the mixture was filtered through a weighed Selas sintered glass crucible and the transfer made quantitative by successive washings of the flask. The mother liquor was then transferred quantitatively to a 500 ml volumetric flask and allowed to come to room temperature. If analyses for chloride ion and total chlorine were to be made, the basic scrub also was transferred to the volumetric flask. The contents of the flask then were made up to volume and the different analyses run.

For the determination of oxalic acid three 100 ml aliquots were transferred to three 250 ml beakers and approximately 3 grams of calcium nitrate tetrahydrate was added. These solutions were heated to a temperature of 80°-90° C. and the oxalic acid precipitated out as the calcium salt by adding 1:1 ammonium hydroxide until the solutions were neutral. The precipitates were allowed to digest overnight, were filtered onto an asbestos mat of a Gooch crucible, and washed with water several times. The crucibles were then transferred back to their respective beakers, the mat broken up, and the oxalate titrated

with standard potassium permanganate according to the method of Kolthoff and Sandell (8).

The ionizable chlorine was determined by taking three 75 ml aliquots and titrating by the Volhard method (8).

The total chlorine was determined by taking three 75 ml aliquots and adding a slight excess of 10 percent NaOH. This basic solution was evaporated to a small volume and transferred to a Parr fusion cup. The transfer was made quantitative by successively washing the contents of the beaker into the Parr cup and evaporating to dryness in an oven at 105 degrees C. The chlorine content was then run according to the standard Parr fusion method and recorded as the total chlorine in the soluble fraction.

The carbon dioxide given off from the reaction was trapped in the scrub apparatus by using 10 percent carbonate free base. The analysis of the trapped carbon dioxide was made according to the method of Kolthoff and Sandell for carbon dioxide in limestone (8). It was necessary to run a blank to correct certain inherent errors in the analysis.

The solid residue separated from the mother liquor was dried at room temperature over calcium chloride until a constant weight was attained. The weights of the two runs were averaged and recorded as the weight used in calculations. The two residues were mixed together and a chlorine content analysis run by the standard Parr fusion method.

RESULTS AND DISCUSSION

In Table 2 are the data pertaining to the solid residue
remaining after various time lengths of reaction. These
figures are all based on two grams of the chlorinated starch
GF-M. Column 1 is the weight in grams of the residue remain-
ing at the given time, and column 2 is its chlorine content
in percent. Column 3 is the number of grams of chlorine
present in the residue and is calculated by multiplying the
values in column 1 by the respective values in column 2 and
dividing by 100. Column 4 is the number of grams of chlorine
divided by the equivalent weight of chlorine and then related
to one mole of the chlorinated starch GF-M. Column 5 represents
the amount of carbon, hydrogen, and oxygen present at the
various times and is calculated by subtracting the values in
column 3 from the respective values in column 1.

Table 3 shows the data pertaining to the soluble products
of degradation at various times. Columns 1, 2, and 3 are the
number of moles of oxalic acid, carbon dioxide, and equivalents
of chlorine formed per mole of GF-M at various lengths of re-
action time. These are all experimental values. However,
columns 4 and 5 are calculated values since it is believed that
they represent more accurate values than those arrived at
experimentally. Table 4 gives only the actual experimental
values. Column 4 is calculated by subtracting the equivalents
of chlorine in the solid residue from the known number of
equivalents of chlorine in the original chlorinated starch.
These calculated values, column 4, represent the total

Table 2. Data pertaining to solid residue.

Time in hours	Grams of solid residue	Percent chlorine	Grams of chlorine	Equiv. of Cl/mole of GF-M	Grams of C,H,O, in residue
0*	2.000	27.14	.543	1.65	1.457
1	.517	44.80	.232	.71	.285
3	.418	46.90	.196	.60	.222
6.5	.364	47.35	.172	.55	.192
12	.300	47.66	.142	.44	.158
24	.245	48.60	.119	.36	.126
48	.193	49.25	.095	.29	.098
72	.157	49.86	.078	.24	.079

*These are the values for GF-M.

Table 3. Data pertaining to soluble products.

Time in hours	Moles of $(COOH)_2$/mole GF-M	Moles of CO_2/mole of GF-M	Equiv. of Cl ion/mole GF-M	Equiv. of total Cl/ mole GF-M*	Equiv. of bound Cl/ mole GF-M*
1	.164	.118	.392	.94	.55
3	.314	.471	.490	1.09	.57
6.5	.391	.609	.581	1.10	.52
12	.518	.829	.688	1.21	.52
24	.548	.966	.731	1.29	.56
48	.574	1.157	.803	1.36	.56
72	.596	1.427	.899	1.41	.51

*Calculated.

Table 4. Experimental values of total and bound soluble chlorine.

Time in hours	Equiv. of total Cl/mole GF-M	Equiv. of bound Cl/mole GF-M
1	.84	.45
3	.97	.48
6.5	1.05	.56
12	1.12	.43
24	1.17	.44
48	1.19	.39
72	1.27	.37

equivalents of chlorine in the soluble fraction. From the total equivalents in solution, the equivalents of ionizable chlorine, column 3, are subtracted. This gives the respective equivalents of carbon bound chlorine present in the soluble fraction, column 5.

The results of the action of nitric acid on the chlorinated starch mixture, GF-M, and on the individual chlorinated starches is undoubtedly very complex in nature and any discussion of these results must be of a qualitative character.

The products formed by this action indicate that both hydrolysis and oxidation have taken place. It is evident from Figs. 2, 3, and 5, that the rate of the overall reaction is rapid in the early stages of degradation, then becomes slow, and finally approaches a steady state. This so called steady state appears to be due to a fraction of the chlorinated starch that is very resistent to both hydrolysis and oxidation.

It can be shown from the values in Table 2 that at the end of one hour 57 percent of the originally bound chlorine has become part of the soluble fraction and, of the original carbon, hydrogen, and oxygen composition, 80 percent has become part of the soluble fraction. In contrast to this, at the end of 72 hours, 86 percent of the chlorine and 95 percent of the C, H, and O composition has become soluble. This soluble fraction from the reaction appears to be one of reaction and not one of mere solubility. Both the author and Thomson (11) have observed the solubility of chlorinated starches in this stage of chlorination and are in agreement that they are insoluble in water; however, the author has recorded them as reactive with water.
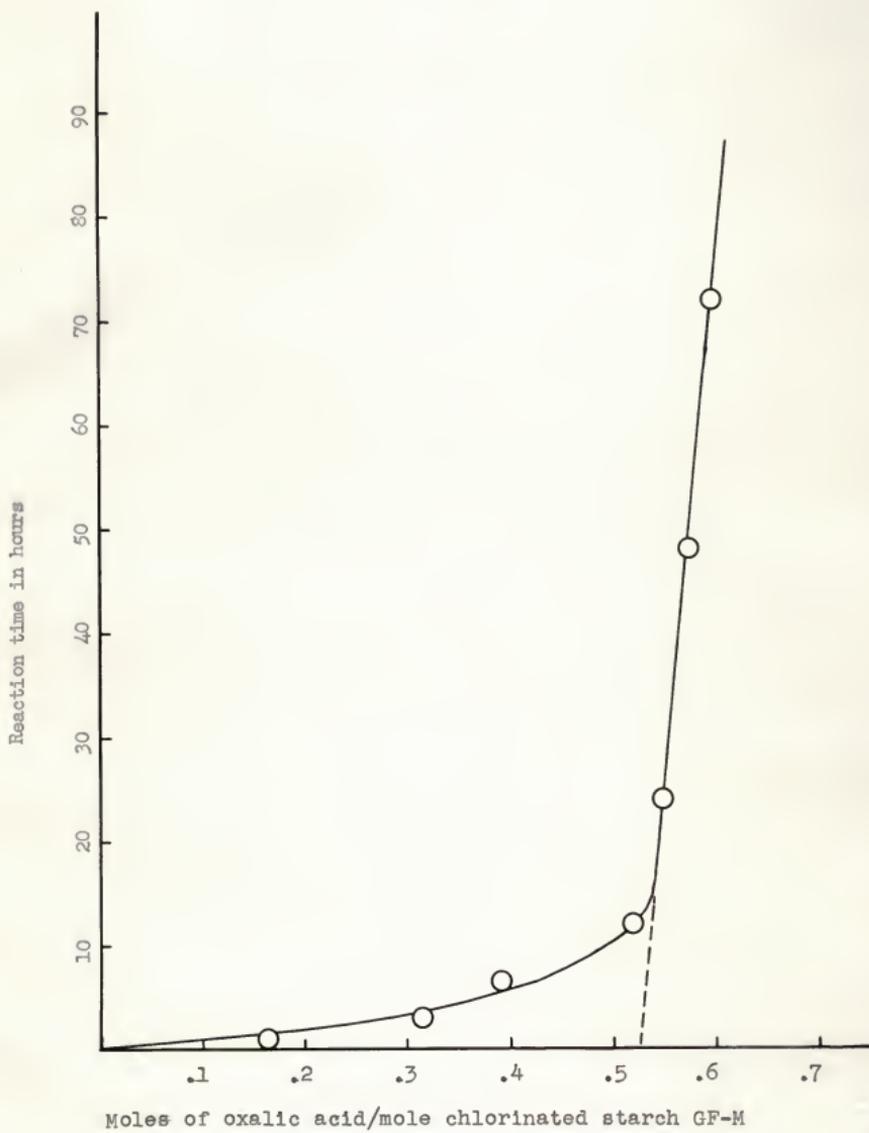
Fig. 2. Concentration of oxalic acid vs time.

In the soluble fraction three of the entities present were identified, and the respective rates of their formation observed. In each case there is observed a rate curve which is apparently the result of at least two distinct and separate rates.

In the time vs oxalic acid formation plot, Fig. 2, it may be noted that the rate of formation proceeds very rapidly in the early stages of the reaction. The rate then decreases slowly up to about 12 hours reaction time, and then decreases very rapidly to a slow rate which remains steady. This constancy of the rate suggests that it might be that of a zero order reaction in which a surface phenomenon limits the availability of the reactive centers to hydrolytic and oxidative attack. Although the data are insufficient at this time to positively identify the order of these two seemingly distinct and separate rates, the break that appears in the rate curve appears to be significant. A discussion of this significance will be discussed later.

The plot of time vs concentration of ionizable chlorine, Fig. 3, has the same characteristics as the oxalic acid plot. The concentration of chlorine increases rapidly at first and, after the reaction has proceeded about 12 hours, slows very rapidly to a seemingly steady state. Here again the reaction appears to approach or assume a zero order.

The plot of bound chlorine vs time is shown in Fig. 4, in which "A" is the experimental curve and "B" is the curve from calculated values. As was mentioned earlier, the values

Equivalents of ionizable chlorine/mole of chlorinated starch GF-M
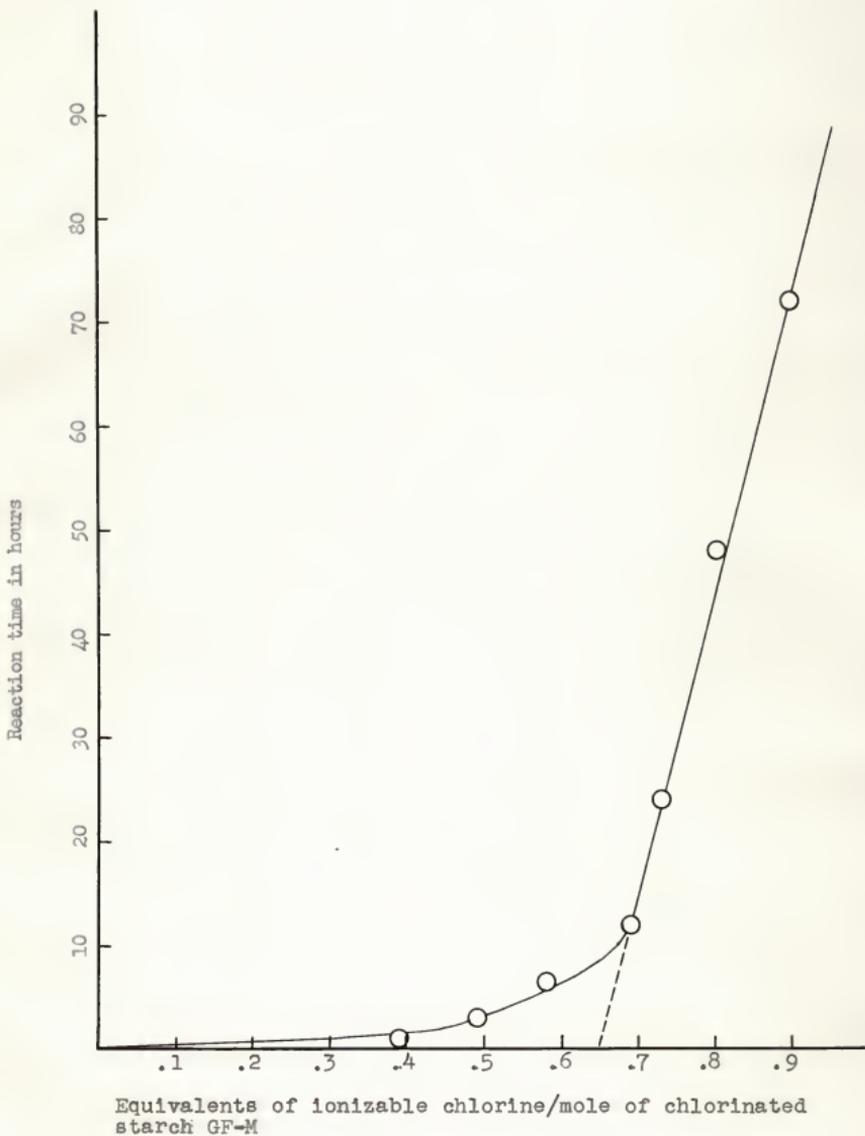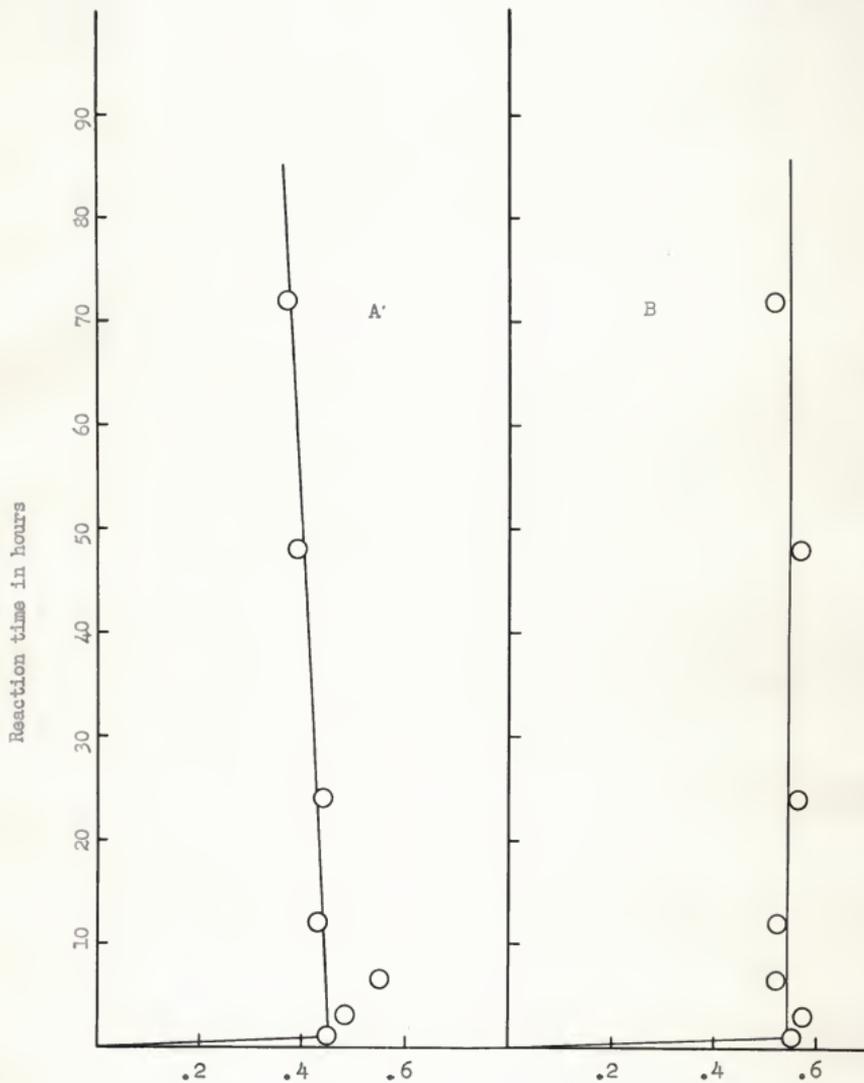
Fig. 3. Concentration of ionizable chlorine vs time.

Equivalents of bound chlorine/mole of chlorinated
starch GF-M. Curve "A" represents experimental values
and curve "B" calculated values

Fig. 4. Concentration of bound chlorine vs time.

for curve "B" were calculated by assuming that the equivalents
of bound chlorine in solution would be the difference between
the equivalents of ionizable chlorine in solution plus the
equivalents of bound chlorine in the residue, and the equiva-
lents of chlorine in the original chlorinated starch mixture
GF-M. This is considered a valid assumption because the experi-
mental values, although poor, indicate the same type curve.
From curve "B", Fig. 4, it is evident that the concentration
of bound chlorine does not change with time and indicates
that this chlorine is bound to carbon in such a manner as to
be unaffected by either hydrolysis or oxidation. However,
its very rapid formation in the earliest stages of the reac-
tion suggests that the fraction of the chlorinated starch con-
taining this chlorine is very susceptible to hydrolysis and
is consequently readily solublized.

Figure 5 is a plot of the concentration of CO_2 vs time.
It shows the same characteristic type of curves as those of
oxalic acid, Fig. 2, and ionizable chlorine, Fig. 3. However,
that part of the curve that might be considered a zero order
reaction has a somewhat faster rate than the other curves.
It is possible that some of the carbon dioxide is coming from
the oxalic acid that has already been produced. The amount
of carbon dioxide is not enough to show that continuous de-
carboxylation has taken place on the glucopyranose ring, since,
if it had, one would expect at least four moles of carbon
dioxide for each mole of oxalic acid produced.

The plot of the amount of C, H, and O residue per unit
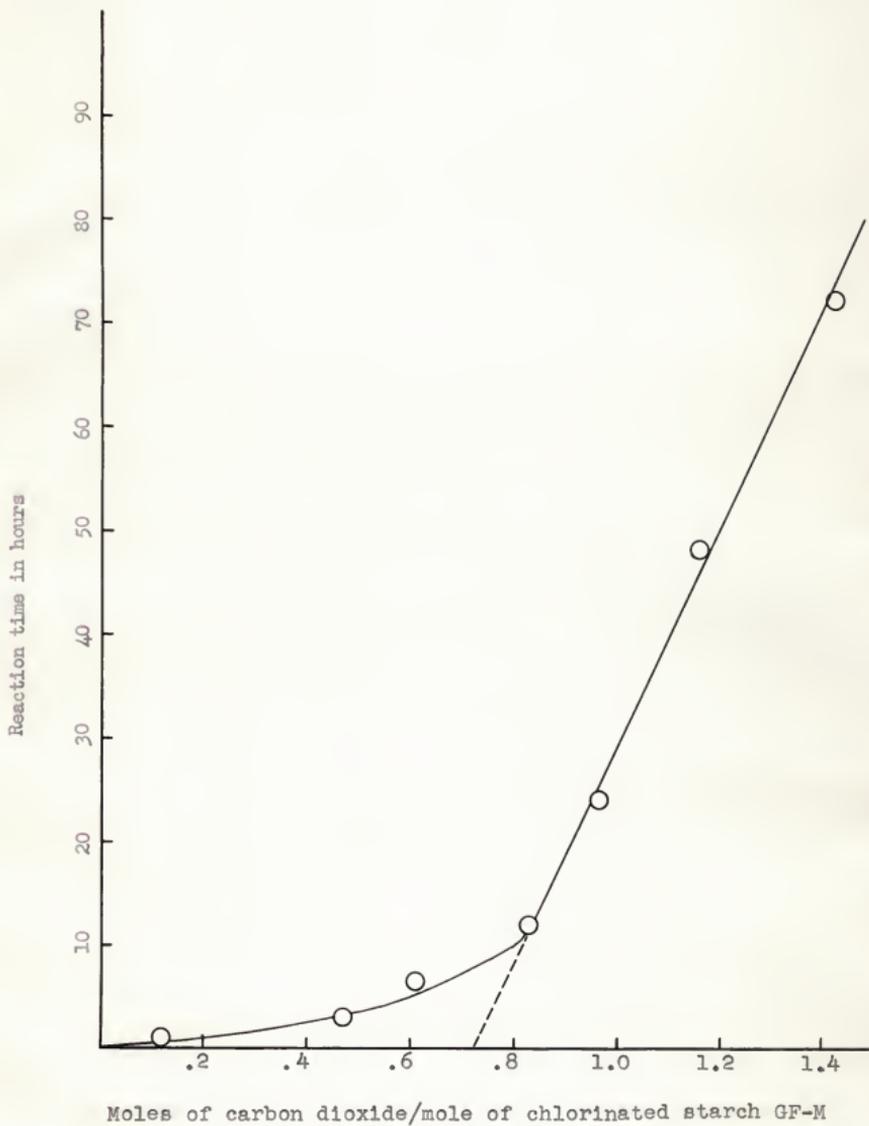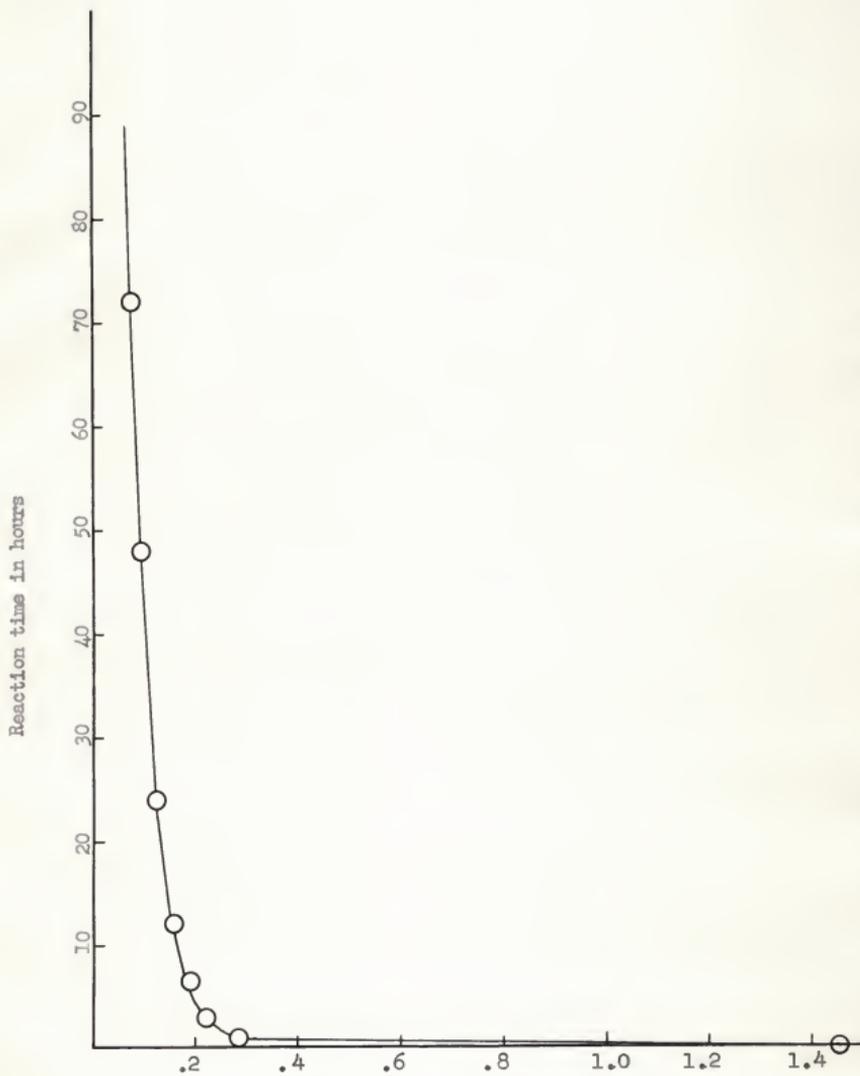of time, Fig. 6, is significant in that it shows a very rapid

Fig. 5. Concentration of carbon dioxide vs time.

Weight in grams of C, H, and O composition of solid
residue and at zero time the weight in grams of
chlorinated starch GF-M

Fig. 6. The C, H, and O composition vs time.

decrease of the C, H, and O in a very short time. As was men-
tioned earlier, at the end of one hour, 80 percent of the
original C, H, and O content has reacted to such an extent
that it is solublized. The remaining 20 percent then under-
goes reaction only very slowly, until after 72 hours reaction
about 5.4 percent of the original C, H, and O composition re-
mains. Also significant here is the fact that the total
residue now contains about 50 percent chlorine.

From these plots of the formation of identifiable products
of degradation it appears obvious that at least two different
fractions, and possibly a third, of the chlorinated starch are
present. The first fraction is one which reacts rapidly bring-
ing about the production of oxalic acid, ionizable chlorine,
and carbon dioxide, and the hydrolysis of the mixture to a
point of solubility. The second fraction is one which stub-
bornly resists both hydrolytic and oxidative degradation. The
third possible fraction would be the fraction that is soluble
but containing tightly bound chlorine. This latter fraction
could be a part of the first. Of these three possible fractions,
that fraction which is the most highly chlorinated resists the
action of nitric acid the most vigorously. This difference in
reactivity exhibited by the chlorinated starch leads to specu-
lation of the structure of the starch granule and the effect
of chlorination upon it.

There is good reason to believe that, of the total ether
oxygen bonds joining the glucose units together in starch,
approximately four percent are 1,6-links*. The chlorination

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*Personal communication from Dr. H. N. Barham. Kansas State
College.

of starch with phosphorus pentachloride (1) and the data therefrom indicate that there is a high incidence of these 1,6-links in the surface of the granule. It is entirely possible that the surface of the granule would be very highly chlorinated in the chlorination process, since eventually it must provide the avenues for inwardly diffusing reactant molecules and thus it would be exposed to the chlorination process both longer and more intimately.

In the chlorination process it is also reasonable to assume that the number six carbon atom of the 1,6-link would have two chlorines attached to it, and the number one carbon atom of this link would have one chlorine attached to it. With these chlorines so grouped, it is probable that this 1,6-link would be very difficult to hydrolyze because of steric considerations. Such a structure is shown in Fig. 7, in which the remaining chlorine atoms attached to the glucose units are in their most probable positions according to previous knowledge of the
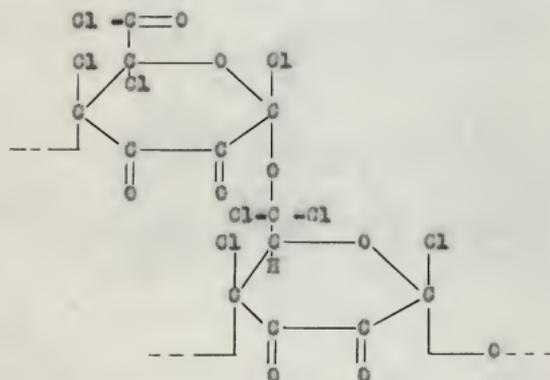

Fig. 7. Possible structure with 1,6 ether link.

chlorination reaction (2). This hypothesized structure in all probability is not so simple as is pictured. It does, however, represent a plausible structure commensurate with the facts known of the solid residue. The solid residue when viewed under a microscope appears to still have a highly organized structure, which indicates that the ring structure of the glucose unit is intact. The yellow color of the residue indicates the continued presence of the α-diketone group. The incidence of the α-diketone in the residue is of course beyond the scope of this thesis, but if the brightness of color is a criterion, the incidence is high. The percent of chlorine calculated for the hypothesized structure is 49.56 percent; the chlorine content of the solid residue by the Parr method was 49.86 percent.

The amount of bound soluble chlorine at any time has an average calculated value of 0.54 equivalents per mole of chlorinated starch GF-M. By assuming that the order of reaction in the later stages of production of oxalic acid is zero order and extrapolating this part of the curve back to zero time, a value of 0.53 mole of oxalic acid per mole of chlorinated starch GF-M is obtained. This extrapolation is shown by a dotted line in Fig. 2. In the ionizable chlorine plot, Fig. 3, and the carbon dioxide plot, Fig. 5, an extrapolation of the curve was made in the same manner as for the oxalic acid plot, Fig. 2. In each case it is assumed that the values obtained in this manner are the approximate amounts of these different substances that are formed from the more easily

Gram equivalents of chlorine in solid residue from
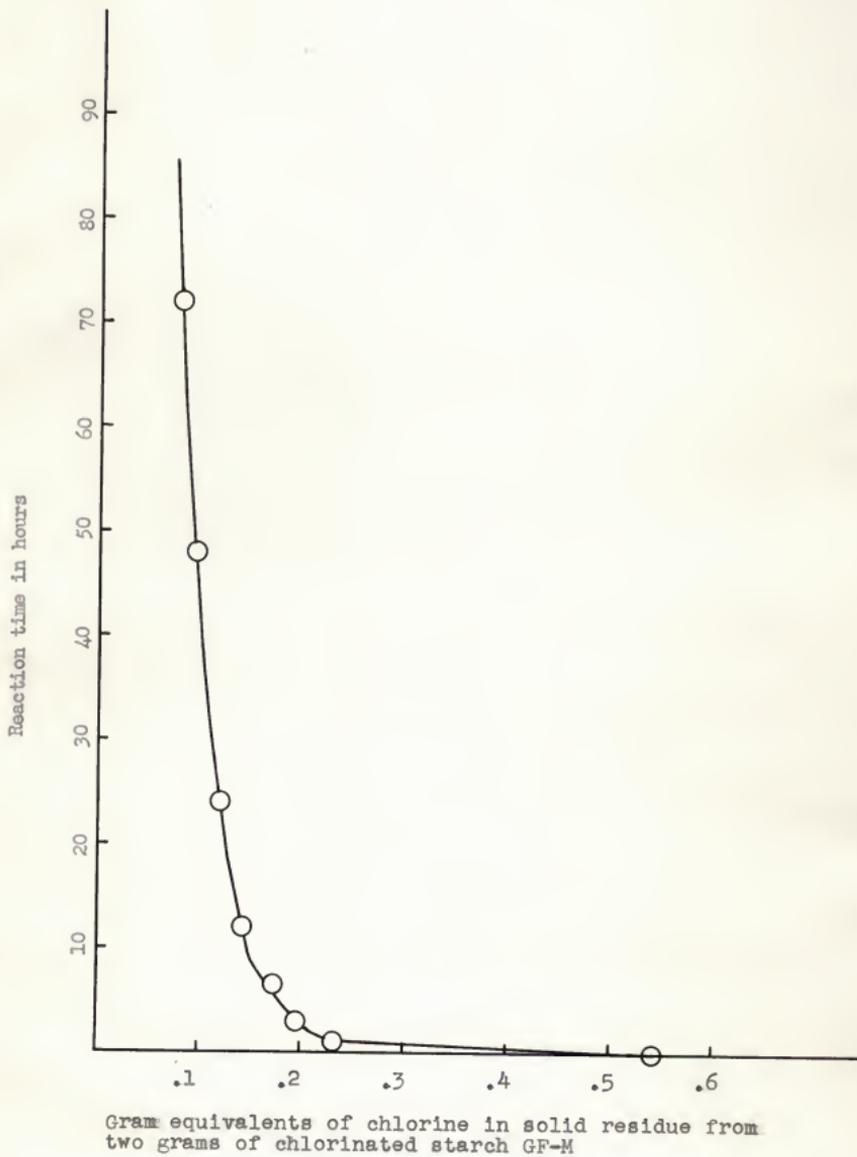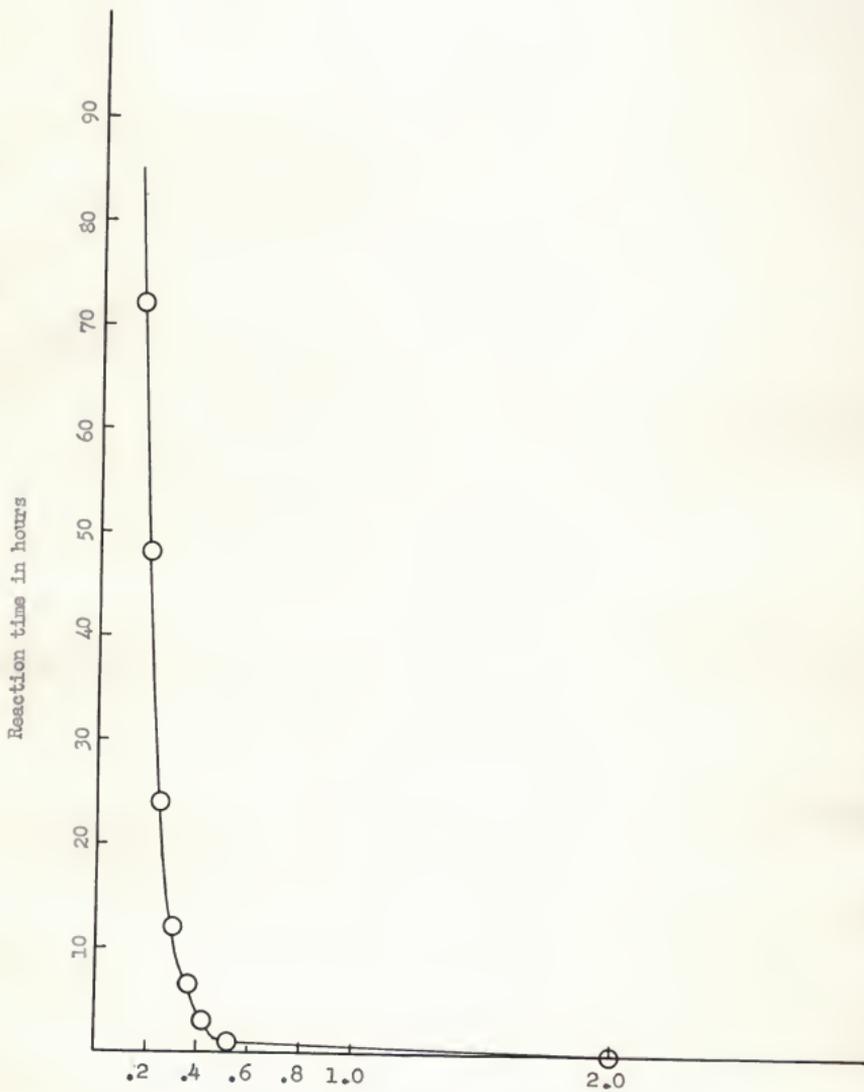two grams of chlorinated starch GF-M

Fig. 8. Grams of chlorine in residue vs time.

Grams of solid residue from two grams of chlorinated
starch GF-M

Fig. 9. Grams of solid residue vs time.

hydrolyzable fraction. These amounts in each case are:
ionizable chlorine, 0.65 equivalents per mole of GF-M; carbon
dioxide, 0.73 mole per mole of GF-M; oxalic acid, 0.53 mole
per mole GF-M. If now the amount of ionizable chlorine and
bound chlorine in solution are added together a value of 1.19
equivalents of chlorine per mole of GF-M is obtained. If it
is assumed that all of the carbon dioxide production comes
about from the same source as the oxalic acid, a value in
terms of oxalic acid can be obtained by dividing the amount of
carbon dioxide by two and adding to the amount of oxalic acid;
this value is 0.9 mole of oxalic acid per mole of GF-M. By
this reasoning the more reactive fraction of the chlorinated
starch mixture GF-M would appear to have a structure contain-
ing approximately one equivalent of chlorine and capable of
yielding approximately one mole of oxalic acid.

However, the structural contribution that seems most
probable to yield oxalic acid is the alpha diketone and if
this is the source of the rapid formation of oxalic acid, a
chlorine bound on the number four position would be unstable.
This reasoning, which seems to be the most probable, would
indicate that the formation of bound chlorine cannot be
directly related to the formation of oxalic acid or ionizable
chlorine but is related to an independent chemical entity that
is formed by the degradation. A possible structure for this
entity is shown in Fig. 10. In order that such a structure
would be soluble, the degree of polymerzation would probably
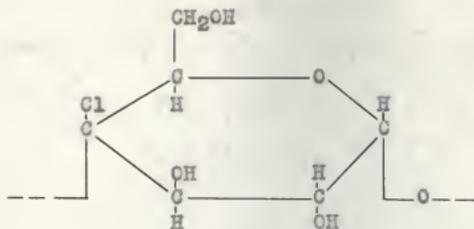have to be small. That such structure with this glucopyranose

Fig. 10. Postulated structure containing bound chlorine.

ring is possible gains support when one considers that if the ring structure underwent carbon to carbon bond scission any carbon bound chlorine would become unstable and would be removed via hydrolysis. That such a structure would resist hydrolysis of the 1,4-ether link is indicated by the fact that if the chlorine atom on the number four position was removed to any other position, hydrolysis of both the chlorine atom and the 1,4-link would occur easily. The experimental evidence, Fig. 4, shows that the bound chlorine is very stable to hydrolysis.

Figures 8 and 9, are plots of the number of grams of chlorine in the solid residue and the number of grams of residue respectively, plotted against time. The curve in Fig. 6, the carbon, hydrogen and oxygen composition vs time, is simply the curve obtained when the curve in Fig. 7 is subtracted from the curve in Fig. 8. From this curve, Fig. 6, it appears that the ultimate degradation of the solid residue is dependent upon the ability of the nitric acid to reach the carbohydrate portion

and not upon its ability to hydrolyze off the chlorines;
however the chlorines may be sterically responsible inasmuch
as their relative bulkiness might block the attack of the
nitric acid.

SUMMARY

The action of 1:1 nitric acid on the chlorine deriva-
tives of starch that has closely approached the dichloride stage
causes hydrolytic and oxidative degradation. More than 90 per-
cent of the latter are degraded in 72 hours reaction time at
70° C.

The action of nitric acid on chlorine derivatives of
starch that have closely approached the dichloride stage and
the kinetics of this reaction appear to be very complex. Rate
curves of the known products of degradation and other rate curves
are shown. The order of these reactions could not be resolved
entirely. However, a portion of each of these curves appears
to be or approach zero order.

The identifiable products of degradation were found to be
oxalic acid, chloride ion, and carbon dioxide. Syrups or dif-
ficulty crystalizable products of degradation were not identi-
fied. That these latter products probably contain very tightly
bound chlorine is discussed and a plausable structure postulated.

Part of the chlorinated starch resists degradation very
vigorously and remains insoluble in the reaction medium. This
solid contains about 50 percent chlorine. Its possible relation

to the gross structure of the starch granule and a plausible
structure involving the 1,6-link are discussed.

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A STUDY OF THE HYDROLYTIC AND OXIDATIVE DEGRADATION
OF SOME CHLORINE DERIVATIVES

by

CALEB MAX STOUT

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AN ABSTRACT OF A THESIS

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The purpose of this study was to further clarify the structure and nature of chlorinated starches that have approached the 6:2 dichloride stage and if possible to apply the findings to the nature of starch itself.

In order to accompolish this a degradative method was employed in which 1:1 nitric acid was the degradation reagent. An attempt to identify all of the products of degradation was made and several of the entities identified. A kinetic study was made by analyzing qualitatively for the amounts of these entities formed at different intervals of reaction time. The data obtained was tabulated and plotted in various ways and from this certain conclusions concerning the chlorinated starches stated.

The action of the nitric acid was both hydrolytic and oxidative. The identifiable products of the degradation were oxalic acid, chloride ion, and carbon dioxide. Syrups or difficultly crystalizable products of the degradation that were not identified were believed to contain very tightly bound chlorine. In this connection a structural possibility is discussed.

There appears to be two and possibly three differently reactive fractions that come from the chlorinated starch as a result of degradation. A discussion of a solid insoluble fraction of 50 percent chlorine content is included.