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 Proclus 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 (3).

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 exhaustively 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 contributed by this laboratory. In 1946, Barham, Stickley, and Caldwell (1) reported the successful chlorination of starch with phosphorus pentachloride, and in 1950 the direct chlorination 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 stability. 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 $\alpha$-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 $\alpha$-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

*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 degradation, 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 unidentified 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 tetrachloride, 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 possibilities 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 chromatographic separation was used. The method of Stark, Goodban, and Owens (10) was used since it would effect the separation of nearly all of the theoretically 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 extraction 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 extraction 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 calculations. The method of these calculations was straightforward 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.

<table>
<thead>
<tr>
<th>Name</th>
<th>Weight (g)</th>
<th>Chlorine (g)</th>
<th>Chlorine (% of weight)</th>
<th>Mole of IHC₃ per Chlorine per glucose unit</th>
<th>Carbonyl glucosyl glucan unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>GF-39</td>
<td>12.214</td>
<td>215.57</td>
<td>27.01</td>
<td>1.537</td>
<td>4.73</td>
</tr>
<tr>
<td>GF-23</td>
<td>13.672</td>
<td>210.72</td>
<td>25.29</td>
<td>1.588</td>
<td>4.68</td>
</tr>
<tr>
<td>GF-19</td>
<td>16.367</td>
<td>218.03</td>
<td>27.78</td>
<td>1.465</td>
<td>4.64</td>
</tr>
<tr>
<td>GF-15</td>
<td>13.154</td>
<td>229.49</td>
<td>31.16</td>
<td>1.372</td>
<td>4.75</td>
</tr>
<tr>
<td>GF-11</td>
<td>14.839</td>
<td>209.13</td>
<td>24.69</td>
<td>1.585</td>
<td>4.62</td>
</tr>
<tr>
<td>GF-M</td>
<td>----</td>
<td>216.28</td>
<td>27.14</td>
<td>1.510</td>
<td>4.68</td>
</tr>
</tbody>
</table>

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. (± .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 throughout the apparatus were made by means of ground glass standard taper joints. The complete apparatus is shown in Plate I.

Two grams of GF-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
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 stop-
cocks were closed. This time was noted and recorded as the
stopping time of the reaction. The reaction vessel was immedi-
ately 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 solu-
tions 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 remaining 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 reaction 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.

<table>
<thead>
<tr>
<th>Time in hours</th>
<th>Grams of solid residue</th>
<th>Percent chlorine</th>
<th>Grams of chlorine</th>
<th>Equiv. of Cl/mole of Ca,H₂O₁₈</th>
<th>Grams of Ca,H₂O₁₈ in residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>0*</td>
<td>2.000</td>
<td>27.14</td>
<td>.543</td>
<td>1.65</td>
<td>1.457</td>
</tr>
<tr>
<td>1</td>
<td>.517</td>
<td>44.80</td>
<td>.232</td>
<td>.71</td>
<td>.235</td>
</tr>
<tr>
<td>3</td>
<td>.418</td>
<td>46.90</td>
<td>.196</td>
<td>.60</td>
<td>.222</td>
</tr>
<tr>
<td>6.5</td>
<td>.364</td>
<td>47.35</td>
<td>.172</td>
<td>.55</td>
<td>.192</td>
</tr>
<tr>
<td>12</td>
<td>.300</td>
<td>47.66</td>
<td>.142</td>
<td>.44</td>
<td>.153</td>
</tr>
<tr>
<td>24</td>
<td>.245</td>
<td>48.60</td>
<td>.119</td>
<td>.36</td>
<td>.126</td>
</tr>
<tr>
<td>48</td>
<td>.193</td>
<td>49.25</td>
<td>.095</td>
<td>.29</td>
<td>.098</td>
</tr>
<tr>
<td>72</td>
<td>.157</td>
<td>49.86</td>
<td>.078</td>
<td>.24</td>
<td>.079</td>
</tr>
</tbody>
</table>

*These are the values for GF-M.
Table 3. Data pertaining to soluble products.

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>Moles of ((\text{GCH})_2)/mole GF-M</th>
<th>Moles of (\text{CO}_2)/mole of Cl</th>
<th>Equiv. of Cl/mole of ((\text{COOH})_2)</th>
<th>Equiv. of total Cl/mole GF-M</th>
<th>Equiv. of bound Cl/mole GF-M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.164</td>
<td>0.118</td>
<td>0.392</td>
<td>0.94</td>
<td>0.55</td>
</tr>
<tr>
<td>3</td>
<td>0.314</td>
<td>0.471</td>
<td>0.490</td>
<td>1.09</td>
<td>0.57</td>
</tr>
<tr>
<td>6.5</td>
<td>0.391</td>
<td>0.609</td>
<td>0.581</td>
<td>1.10</td>
<td>0.52</td>
</tr>
<tr>
<td>12</td>
<td>0.518</td>
<td>0.829</td>
<td>0.688</td>
<td>1.21</td>
<td>0.52</td>
</tr>
<tr>
<td>24</td>
<td>0.548</td>
<td>0.966</td>
<td>0.731</td>
<td>1.29</td>
<td>0.56</td>
</tr>
<tr>
<td>48</td>
<td>0.574</td>
<td>1.157</td>
<td>0.803</td>
<td>1.36</td>
<td>0.56</td>
</tr>
<tr>
<td>72</td>
<td>0.596</td>
<td>1.427</td>
<td>0.899</td>
<td>1.41</td>
<td>0.51</td>
</tr>
</tbody>
</table>

*Calculated.

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

<table>
<thead>
<tr>
<th>Time in hours</th>
<th>Equiv. of total Cl/mole GF-M</th>
<th>Equiv. of bound Cl/mole GF-M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.84</td>
<td>0.45</td>
</tr>
<tr>
<td>3</td>
<td>0.97</td>
<td>0.48</td>
</tr>
<tr>
<td>6.5</td>
<td>1.05</td>
<td>0.56</td>
</tr>
<tr>
<td>12</td>
<td>1.12</td>
<td>0.43</td>
</tr>
<tr>
<td>24</td>
<td>1.17</td>
<td>0.44</td>
</tr>
<tr>
<td>48</td>
<td>1.19</td>
<td>0.39</td>
</tr>
<tr>
<td>72</td>
<td>1.27</td>
<td>0.37</td>
</tr>
</tbody>
</table>
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-N, 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 resistant 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.
Moles of oxalic acid/mole chlorinated starch GF-M

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 equivalents of chlorine in the original chlorinated starch mixture GF-M. This is considered a valid assumption because the experimental 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 reaction suggests that the fraction of the chlorinated starch containing 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 decarboxylation 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.

Moles of carbon dioxide/mole of chlorinated starch GF-M
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 solubilized. 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-
main. 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

*Personal communication from Dr. H. N. Barham. Kansas State
College.
of starch with phosphorus pentachloride (1) and the data there-
from 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 ex-
posed 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.](image)
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 $\alpha$-diketone group. The incidence of the $\alpha$-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 OP-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 OP-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.
10
20
30
40
50
60
70
80
90

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, 0.75 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 polymerization 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 derivatives of starch that has closely approached the dichloride stage causes hydrolytic and oxidative degradation. More than 90 percent 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 difficulty crystalizable products of degradation were not identified. That these latter products probably contain very tightly bound chlorine is discussed and a plausible 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
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by

CALEB MAX STOUT

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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 accomplish 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 crystallizable 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.