

A STUDY OF THE CHEMICAL PROPERTIES OF
SOME CHLORINE DERIVATIVES OF STARCH

by

JOSEPH JUNIOR BRYSE

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INTRODUCTION

Very little is known about the chemical behavior of starch and its derivatives. Starch has been known for ages but owing to its peculiar inertness it has not been widely used in industrial development like many other plant materials such as vegetable oils, cellulose and plant proteins. The great quantities of starch which are utilized in industry are used either without chemical change or as simpler modifications and degradation products.

Our present sources of such organic raw materials as coal and particularly petroleum may some day be exhausted, but a plant material such as starch is a raw organic material which can be replenished indefinitely. Norman F. Kennedy, director of research for the Corn Industries Research Foundation has said, "In recent years industry has become certain that its future expansion will depend largely on the chemical uses which can be developed from starch as an organic raw material." It is toward this goal that we are striving.

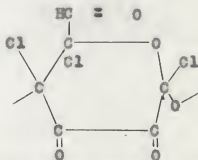
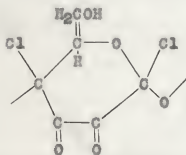
It is well known in organic chemistry that most halogen derivatives are usually very reactive and undergo a large number of reactions to give many more derivatives. It may be assumed, therefore, that the successful halogenation of starch would provide reactive intermediates which would be convertible into many useful substances of diverse character.

The starch laboratory of the Chemistry Department of Kansas State College has been engaged for some time in a

study of the possibilities of indirect and direct chlorination of starch. Dr. H. N. Barham and co-workers^{*} have succeeded in preparing both indirectly and directly chlorinated starch derivatives. The next logical step is to study the properties of these products to effect their eventual utilization.

The work reported herein is concerned only with the products formed by the direct chlorination of starch. Since these products have never been synthesized before there is no literature on the subject. H. N. Barham, R. A. Olson, D. H. Olson, E. S. Stickley, H. S. C. Lau, and T. R. Thomson have worked on the methods and conditions suitable for the formation of these products but there has been heretofore no formal study of the physical and chemical behavior.

It has been found in kinetic studies that by varying reaction conditions the chlorination can be so controlled that steady states seem to be reached wherein two, three, four and six atoms of chlorine are present in each glucose residue. The compounds having two and three chlorine atoms per glucose residue have been assigned the following formulas on the basis of the changes which occur during their formation.



^{*}Personal communication of unpublished data.

Combustion analysis and certain type reactions further confirm these formulas.

The changes which occur during the preparation of these di- and tri-chlorinated starches, and the physical characteristics of the materials themselves indicate that very little, if any, degradation of the starch molecule has taken place. It may be assumed, therefore, that the molecular aggregation of glucose units in these chlorinated products does not differ materially from that of the starch itself. Accordingly, the chlorinated products may be properly regarded as mixtures similar to those known to have plastic properties. Starch, however, does not appear to possess a structure which enables it to be used in making plastics of good quality. Since the skeleton of the chlorinated starch molecules is probably much the same as that of starch, the molecules also possess poor plastic forming properties and their structure would need to be modified before they would be suitable for that purpose. A rupture at some point in the six atom ring would possibly so modify the chlorinated starch molecules that it would be suitable as a plastic material. The most likely point for the rupture of this ring is the bond between carbon atoms two and three. These carbons are a part of a 1,2 or α -diketone structure. Weitz and Scheffer (6) have found that the bond between the carbonyl groups of an α -diketone may be ruptured by means of alkaline hydrogen peroxide with the subsequent formation of carboxyl groups. When the attempt was made to carry out a similar reaction with the α -diketone structure

of the chlorinated starches, hydrolytic changes were so extensive that no products have so far been isolated therefrom.

These chlorinated products possessed an odor of hydrogen chloride and also their own distinctive odor. Apparently these materials reacted with the moisture of the air and formed hydrogen chloride in a manner characteristic of aliphatic acid chlorides. This reaction naturally caused a decrease in the chlorine content of the samples.

The work reported upon in this thesis deals with a study of the susceptibility of the chlorinated products to hydrolysis and of the acidic character of the products of hydrolysis. The color of these substances in aqueous solution made the usual titrations with indicators infeasible. Inasmuch as the work would involve the handling of a mixture of acids together with a reducing agent, the method of conductimetric titration was applied in preference to several other physicochemical methods that might otherwise been used.

MATERIALS AND METHODS

The chlorinated starch derivatives used were made in this laboratory either by H. Lau or by T. Thomson in the course of a study of the liquid phase chlorination of starch. These products contained varying amounts of chlorine bound to carbon depending upon the conditions under which they were made and stored. Examinations were made only of the trichloride, dichloride or products of lesser chlorine content.

The only product which could be considered a true di-chloride as originally formed is that designated as T-11. At the time this material was prepared it contained 30.32 percent chlorine.* L-8 contained 27.97 percent chlorine when prepared, while L-13 contained 23.86 percent chlorine. A series of five products were studied. These were prepared by T. Thomson in a series of runs at 70° C for varying lengths of time. In addition to this series, other materials, made by different operators and under widely different conditions, were studied. Satisfactory correlations were possible within the above mentioned series but not among the miscellaneous samples.

During the time these samples were stored after preparation, all of the products had undergone some change and loss of chlorine. They were yellowish to dark brown in color and retained the outline of the starch granule as observed under the microscope. They all have an odor characteristic of these products and some of them had admixed with this the odor of hydrogen chloride. Before titration, each sample was set for a suitable time in a vacuum desiccator over soda-lime to remove the odor of hydrogen chloride. Samples for chlorine analysis were taken at the same time the sample for titration was taken and all calculations are based upon the value for the chlorine content obtained in this way.

The water used in the preparation of all solutions was distilled water which had been boiled for about half an hour to remove dissolved gases. This water had a specific

*Analyses by Mr. Thomson

conductance of about 1×10^{-6} mho. According to Kendall (1,2), equilibrium water with air has a specific conductance of 0.8×10^{-6} mho. The conductivity of the water remained constant in the laboratory. No correction for the conductance of the water was made when working with solutions concentrated enough to have a specific conductance of 0.5×10^{-3} to 1×10^{-3} mho.

The standard base solution for titrations was made by dilution of a saturated solution of sodium hydroxide which had been filtered free of carbonate. The normality of this solution was checked by titrating into a standard acid solution made by dilution of reagent grade hydrochloric acid. The sodium chloride solution was made by dissolving a weighed amount of dried analytical reagent salt. The normality of the two latter solutions was checked by precipitating a known volume with silver nitrate solution and weighing the precipitate. Each of these three solutions was adjusted in normality to 0.1000 ± 0.0003 normal. Analytical reagent grade potassium chloride was heated to a red heat to remove all moisture. When cool 1.4918 g were made up to 1000 ml at 20°C to form an exactly 0.0200 N solution which has a specific conductance of 0.003036 mho at 30°C (4).

The benzoyl chloride, acetyl chloride and s-dichloroacetone used were all Eastman white label quality.

The cell used for the conductivity measurements was developed especially for these experiments. Since agitation

and addition of the titrant required considerable volume, an ordinary 400 ml pyrex beaker served as the container. A glass stirring propeller actuated by an electric motor or an air driven turbine was used to keep the solids in suspension and give maximum effect to the added titrant.

Dipping into the liquid in the beaker were the two electrodes which were those of an Ostwald type conductivity cell the cup of which had been replaced by a glass shield perforated by two holes on the side to allow ready circulation of solution. The two holes of the shield were carefully placed when the electrodes were arranged in the beaker so that they faced toward the center of the beaker and the stirring paddles. It was found that the shielded electrodes could be removed from the cell as a unit and replaced in this way without changing the resistance capacity of the total cell.

The conductance of this cell was measured by means of a Wheatstone bridge capable of giving values over a fair range and to three significant figures. The bridge was constructed of a circular slide wire, a dial resistance box, a tapping key, and an A. C. galvanometer, all made by Leeds and Northrup Co., Philadelphia. The current supply for the bridge was ordinary 110 volt, 60 cycle, alternating current stepped down to 15 volts.

Since temperature is such an important factor in the conductivity of solutions, the cell in which the titrations were carried out was set in a constant temperature water bath. This bath was sold by the Precision Scientific Company and was

capable of maintaining a constant temperature to within $\pm .010^\circ \text{C}$. The temperature used was 30°C .

At the time that the sample was weighed out for titration, samples were weighed out for chlorine analysis. The analysis for chlorine was run by fusion with sodium peroxide in a Parr bomb in the presence of sucrose and potassium nitrate, according to the standard procedure as given in their manual (4). The chloride of the resulting solution was determined gravimetrically. The analyses were run in duplicate and the values given in the tables are the averages of the two values.

Before each titration the cell was set up and 200 or 220 ml of conductivity water was placed in the cup. The conductance of the water was checked to make sure that there was no contamination. If the conductivity of the water and the temperature were satisfactory, the sample was weighed out on the analytical balance and placed immediately into the water. The solution was allowed to stir at constant temperature with occasional checking of the conductance until it had come to a steady state. At this point the titration was begun with addition of base and readings taken at regular intervals. It was found that if each conductance measurement was made two minutes after the addition of one milliliter of base, the base had been given sufficient time to react. Immediately after making one reading another portion of base was added and the process repeated.

The value of an unknown conductance, C , can be found with a Wheatstone bridge when it is in balance by the equation

$$C = \frac{1000-H}{HR}$$

in which R is the reading of the resistance box and H is the slide-wire reading. The specific conductance, L, being the conductance of one centimeter cube, is merely the product of the conductance, C, and the resistance capacity, K, of the cell used.

$$L = KC = \frac{K(1000-H)}{HR}$$

Since, during titration, water is added along with the base, the concentration does not increase as rapidly as it would if the base alone were added. Righellato and Davies (5) suggested that the values of the conductance be corrected for this dilution by means of the factor

$$\frac{\text{total volume of solution}}{\text{original volume of solution}}$$

so that the final value which is plotted against the volume of added alkali is

$$\frac{K(1000-H)}{HR} \cdot \frac{\text{total volume of solution}}{\text{original volume of solution}}$$

The value of the resistance capacity of the cell was obtained by pouring the .0200 N potassium chloride into the cell, allowing it to come to temperature equilibrium and then measuring the conductance. This solution was poured out and the cell refilled with fresh solution and the process repeated until the conductance became constant. The resistance capacity was then calculated from the equation

$$K = \frac{.003036 \text{ HR}}{(1000-H)}$$

The salt line was obtained by titrating a quantity of pure water with the .1000 N sodium chloride solution. When the value

$$\frac{K(1000-H)}{\text{HR}} \cdot \frac{\text{total volume of solution}}{\text{original volume of solution}}$$

was plotted against the volume of added solution, a straight line results. Since the volumes of the solutions titrated with the base were never the same as those of the sodium chloride solution the ordinates of each point were corrected again by a factor

$$\frac{\text{volume of NaCl solution}}{\text{volume of acid-base titration}}$$

before superimposing the salt line upon the graph containing the titration curve.

The data obtained by the titration of a sample with standard base give a curve as shown in Figure 6. The slope of the curve on the far left hand side is characteristic of the titration curve of a strong acid with a strong base as shown in Figure 1. The straight line on that side was extended past the minimum of the curve and the intersection of this line with the salt line occurs at the endpoint of the titration. The abscissa of this point gives us the total amount of strong acid present in the solution.

Since there is no sharp break in the starch chloride titration curves to indicate a definite endpoint, a different method of determining the equivalence point must be used.

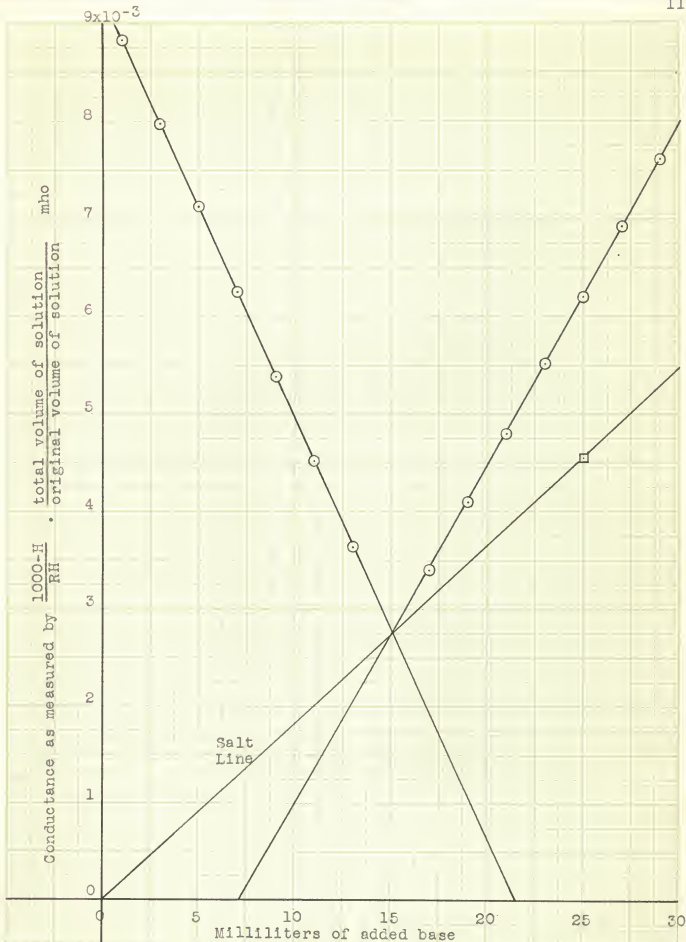


Fig. 1. Titration of a strong acid with a strong base.

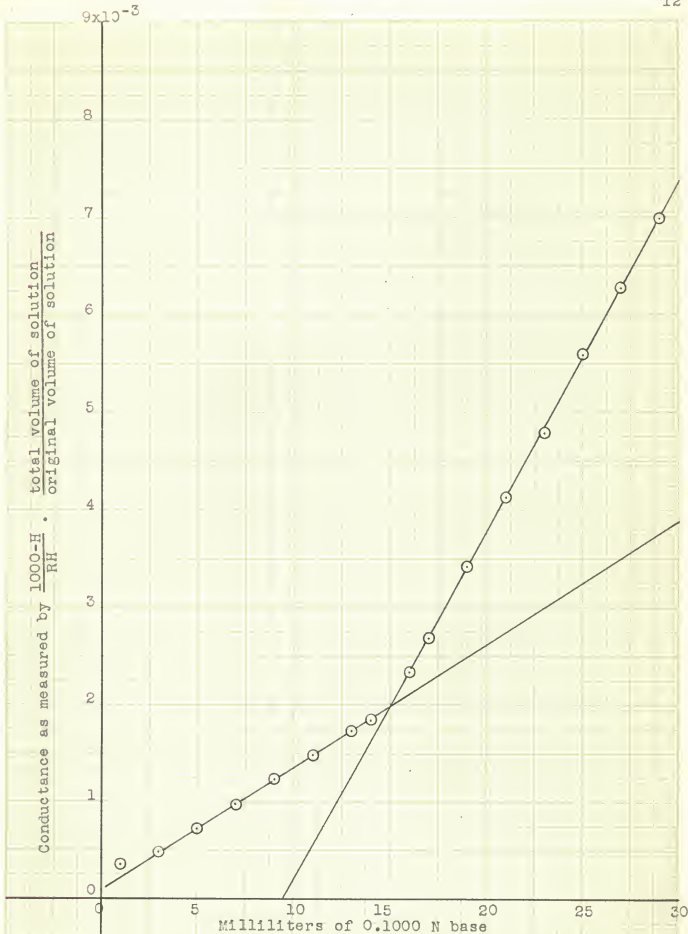


Fig. 2. Titration of a weak acid with a strong base.

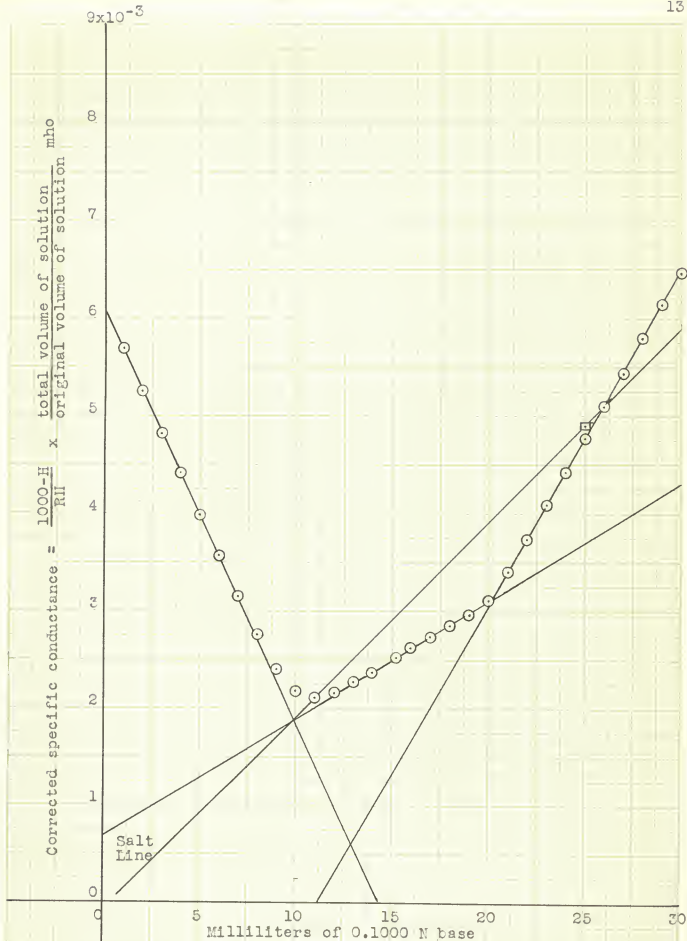


Fig. 3. Titration of a mixture of strong and weak acids with a strong base.

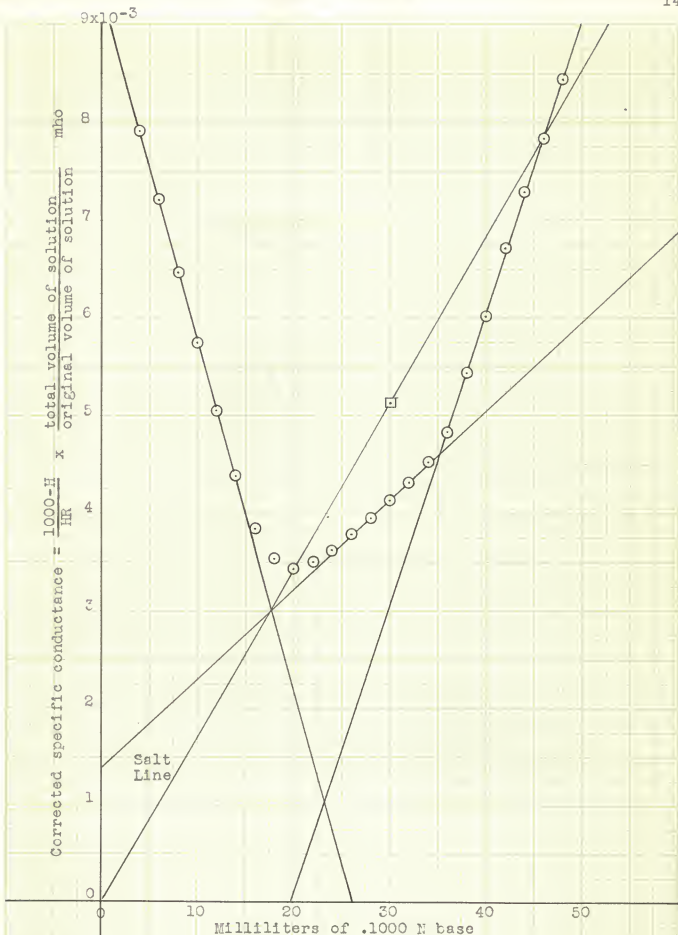


Fig. 4. Titration of benzoyl chloride with strong base after it has reacted with water.

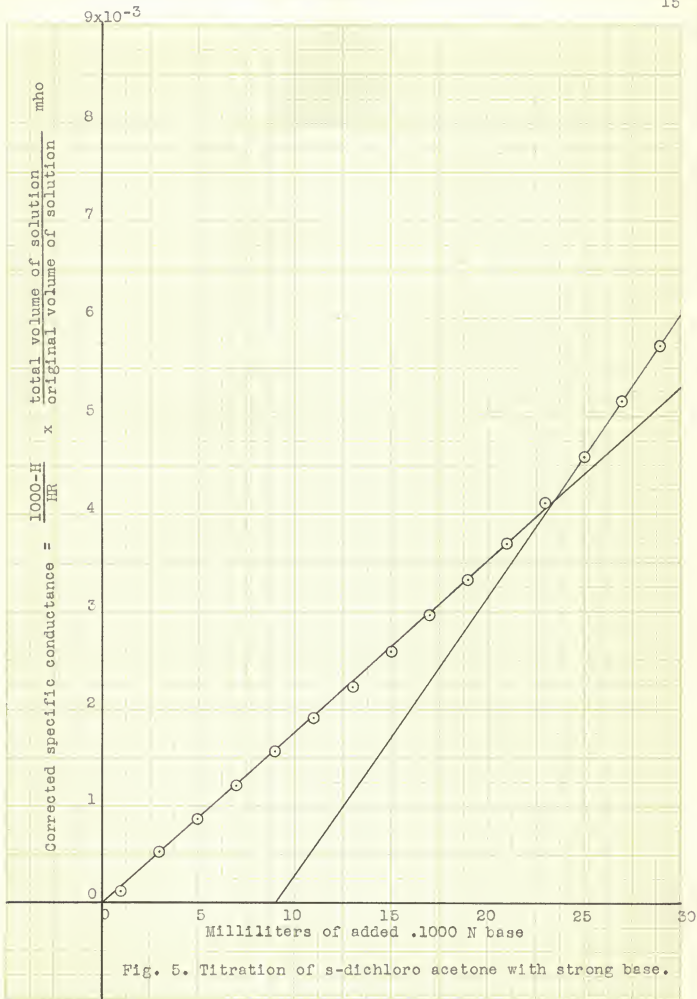


Fig. 5. Titration of s-dichloro acetone with strong base.

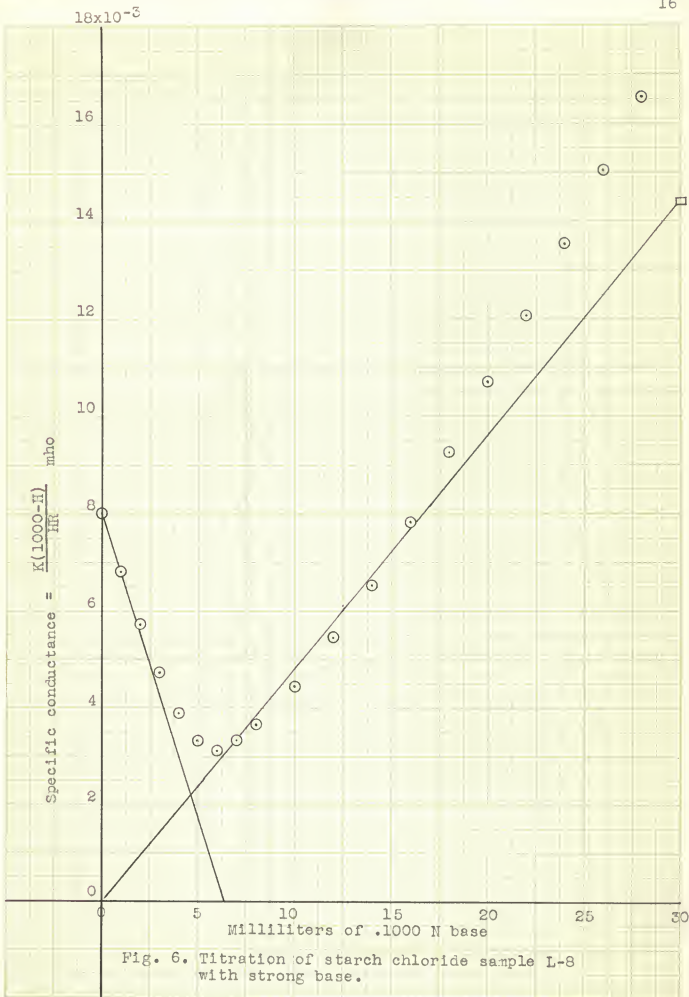


Fig. 6. Titration of starch chloride sample L-8 with strong base.

According to Kolthoff (6), a strong acid can be determined in the presence of a weak acid by the use of a salt line. The steep slope of the curve at the beginning indicates the presence of a strong acid; undoubtedly this is hydrochloric acid. The rounding of the bottom of the curve and the reluctance of the ascending part to reach soon the typical slope of sodium hydroxide added to a neutral solution indicates the presence of one or more complicating factors.

In an attempt to determine the nature of these factors, conductimetric titrations were run on other chlorine containing compounds in which the chlorine was known to hydrolyze off with water. Alkyl halides do not dissolve and do not hydrolyze. Acetyl chloride hydrolyzes very rapidly in water evolving heat and forming a solution of an equivalent mixture of acetic acid and hydrochloric acid. When this is titrated it gives a titration curve exactly the same as a mixture of acids. Benzoyl chloride is also an acid chloride but is one which does not react so rapidly with water. When placed in water and the titration begun immediately, the curve is rounded as in Figure 6. If the conductance is allowed to come to equilibrium before titration the curve obtained is that of Figure 4, or a typical curve of a mixture of a strong and weak acid. When the titration is run while the hydrolysis is still continuing the effect of hydrolysis causes the displacement of the points along the curve so that it is lower and more rounding.

Since the starch chlorine derivatives are apparently α -chloro ketones, a simple organic molecule of similar

structure was selected for comparison. The compound selected was s-dichloro acetone which is soluble in water but which, when in aqueous solution, shows only slight increase in conductance above that of pure water. This indicates that the chlorine atoms are not hydrolyzed off by water alone. The conductance increases as titration with sodium hydroxide takes place. When the data were plotted as before the resulting curve, as seen in Figure 5 consisted of two straight lines intersecting at an obtuse angle. The intersection point is precisely at the point wherein two equivalents of base were added for every mole of the s-dichloro acetone. Evidently the chlorine atoms are hydrolyzed off but not by water alone as with the acid chlorides but by the base present which forms sodium chloride and an alcohol hydroxyl group. When all the chlorine was hydrolyzed off the slope then changed to that characteristic of the addition of sodium hydroxide to a neutral solution.

RESULTS

Upon addition of a sample of a chlorine derivative of starch to water the conductance of the solution showed a sudden increase. The conductance continued to enlarge slowly but at a decreasing rate. When finally the conductance came to a steady state, i.e., when the change in conductance became negligible with time, the reaction with water had gone to completion or had come to equilibrium.

At this equilibrium or completion point the titration was begun. The plot of the specific conductance corrected as noted for dilution versus the amount of added reagent is a rounded curve as shown in Figure 6.

The data for several miscellaneous products are given in Table 1. Table 2 includes the data for the series of products made at 70° C for varying lengths of time. In these tables the degree of substitution has been calculated by means of the equation

$$\frac{35.5 y}{R + 35.5} = x$$

In this equation, x is the fraction of chlorine in the material, y is the degree of substitution, 35.5 the atomic weight of chlorine and R the molecular weight of the anhydro glucose residue stripped of all chlorine. R can be determined with sufficient accuracy from the chlorine analysis data.

The column "fraction reactive" contains the values for the fraction of the total chlorine which reacts rapidly with water. It is simply the ratio of the number of equivalents of acid hydrolyzed off as shown by the intersection of the acid line and the salt line on the graphs to the total number of equivalents of chlorine as calculated from the percentage in the sample. The "fraction non-reactive" is that fraction of the total chlorine which does not hydrolyze with appreciable velocity in the presence of water alone and is merely one minus the value for the fraction reactive.

Table 1. The reactive and non-reactive chlorine in miscellaneous samples of starch-chlorine derivatives.

Name of sample:	Percent of chlorine:	Degree of substitution:	Fraction of chlorine re-active:	Fraction of chlorine non-reactive:	me. non-reactive Cl
:	:	:	active	reactive	me. of starch in sample
L- 8	25.8	1.53	.42	.58	.88
L-13	20.0	1.10	.50	.50	.55
T-11	28.8	1.78	.44	.56	1.00
T-15	40.0	2.93	.61	.39	1.03

Table 2. The relation of time of reaction at 10° to fraction reactive and non-reactive chlorine in starch chlorine derivatives.

Name of sample:	Time reacted: hours	Percent of chlorine:	Degree of substitution:	Fraction of chlorine re-active:	Fraction of chlorine non-reactive:	me. non-reactive Cl
:	:	:	active*	active	reactive	me. of starch in sample
T-28	7 1/3	3.82	0.175	.40	.60	.056
T-24	10 3/4	19.9	1.03	.52	.48	.50
T-23	12	21.8	1.22	.59	.41	.49
T-22	16	23.2	1.33	.61	.39	.51
T-26	24	28.2	1.73	.69	.31	.53

*Value has been corrected for adsorbed HCl.

The figures given in the column headed

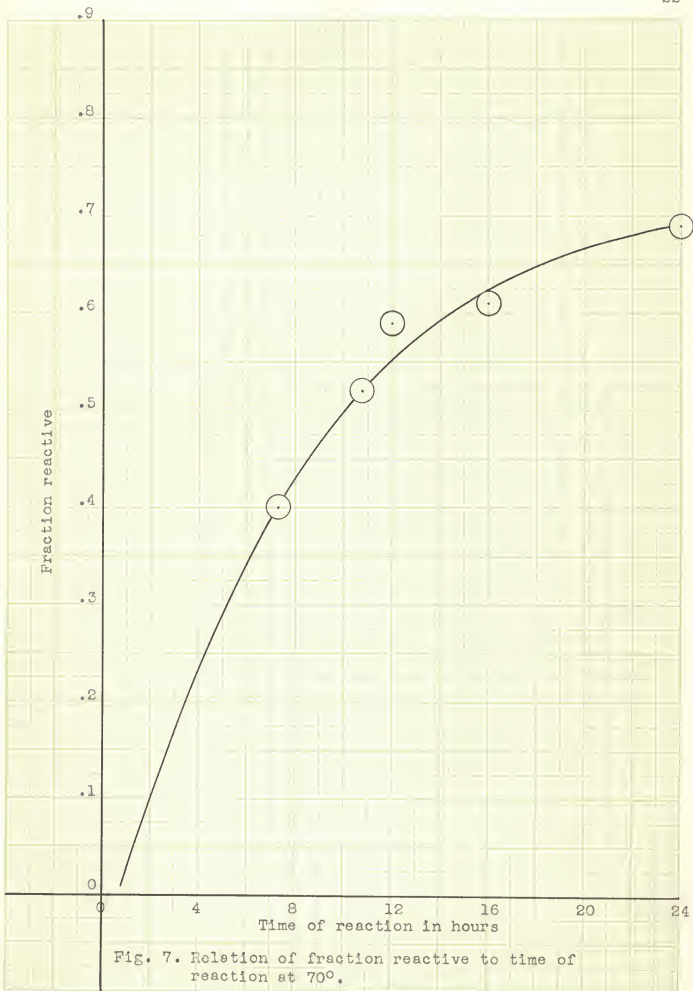
$$\frac{\text{me. non-reactive chlorine}}{\text{me. of starch in sample}}$$

have been calculated by dividing the milliequivalents of non-reactive chlorine by a figure obtained by dividing the difference between the milligrams of sample used and the milligrams of chlorine in that sample by R.

These results show that the relation of the non-reactive chlorine to the number of moles of product used remains almost constant with only slight increase with time. Likewise, it appears from the curve, Figure 7, that the reactive fraction of the chlorine in the sample increases at a decreasing rate with time. The full significance of this is now being studied and will be included in a later communication from this laboratory.

From these observations it is not unreasonable to conclude that part of the chlorine atoms upon the glucose residue are more reactive than others. Obviously some react to give hydrochloric acid and a starch derivative and other chlorine atoms do not hydrolyze in neutral solution but may react with a base to give a salt and a second starch derivative.

If we draw the tangent to the curve at its left hand edge in a straight line we get the curve that hydrochloric acid would have followed if it were alone in water solution being titrated with sodium hydroxide. Where this line and the salt line intersect is therefore the equivalence point of the water reactive chlorine. The difference between this amount of



chlorine and the total amount of chlorine in the sample is the amount of chlorine not hydrolyzed by water alone but hydrolyzed in the presence of base.

Thus it can now be said that there are at least two chlorine atoms in the glucose residue differing in their reactivity with water. Furthermore a quantitative measure of their amounts in any given sample is possible.

Speculation only is possible as to the factors causing the rounding of the curve. It may be that the non-reactive portion of the chlorine is more readily hydrolyzed off in the presence of a higher concentration of base present in the solution after the neutralization of the free acid. This effect alone would be similar to that of the hydrolyzable chlorine in *s*-dichloroacetone, Figure 5. Also possible is the presence of one or more weak organic acid of which a variety are possible. If any one factor comes into play alone in the titration it will appear as a linear portion in the total titration curve. But if more than one factor are acting simultaneously the resulting curve should be of higher degree than the first and therefore not a straight line.

Since the region in the titration curve of these starch chlorine derivatives beyond the endpoint does not reach linearity for some distance, it can be concluded that more than one acidic factor is in effect. One factor will be the hydrolysis of the chlorine from the molecule and the other factor or factors would include the neutralization of any weak

acids present. There are not yet sufficient data to allow a measurement or estimation of the relative extent of any one of these latter factors.

The samples designated at T-11 in Table 1 and as T-26 in Table 2 are almost identical in degree of substitution but are not comparable in fraction of the chlorine reactive. Also, T-22 compares with T-11 in fraction of the chlorine reactive but not in degree of substitution. We know that the samples shown in Table 1 were not prepared under the same conditions, while all the conditions but time were held constant in the preparation of the samples for Table 2. It would seem that the conditions of preparation control to a great extent the relative amounts of chlorine reactive and non-reactive. At the very beginning of the reaction there are three possible positions of attack for the oxidation, namely, the three alcohol groups, each with its own rate of reaction. The molecule is progressively altered as the reaction proceeds, and it may be expected that the rates of oxidation of the remaining alcohol groups on these altered glucose residues will be different than they were originally. Consequently, as the reaction proceeds, twelve different oxidations, each possibly with its own rate, will have developed. The various conditions of preparation could vary the rates of any or all of these oxidations. The data now available will not permit speculation on the effect of the reaction conditions on any one of the partial reactions.

SUMMARY

Starch chlorine derivatives are acid in character and can be titrated with base if conductimetric methods are used.

More than one acidic substance or factor are present and probably three or more as shown by the rounding nature of the curves.

At least one of these can be measured, i.e., the acid formed by the more easily hydrolyzed chlorine.

A measure of the portion of the chlorine that is not reactive can be made by subtraction of the portion reactive from the total chlorine by analysis.

This non-reactive fraction appears to correspond to one chlorine atom per two glucose residues for those samples which were formed in a series of runs at 70° C but for various times of reaction.

In this series of runs at 70° C the fraction that is reactive increases with a decreasing rate with time.

It is possible that the two secondary carbinol groups are oxidized at equal rates and immediately thereafter chlorine is substituted in the α position to the ketone, up to the point where one is oxidized in each glucose residue. Thereafter their rates vary, the one which is the more reactive with water is formed the more rapidly.

No correlations are practicable using data on miscellaneous samples prepared by various operators under a variety of reaction conditions.

ACKNOWLEDGMENTS

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