

## Kinetics and Mechanism of Oxidation of Starch with Sodium Hypochlorite

K. F. PATEL, H. U. MEHTA, and H. C. SRIVASTAVA, *Ahmedabad Textile Industry's Research Association, Ahmedabad 380015, India*

### Synopsis

Kinetics of heterogeneous oxidation of starch with hypochlorite were studied under varying conditions of temperature, pH, buffer components, buffer concentration, and concentration of substrate and oxidant. The kinetic data show that the reaction is first order with respect to hypochlorite. A plot of first-order rate constant for varying starch concentrations versus starch concentration is linear. The rate of oxidation of starch is highest at pH 7.0 and decreases with increasing acidity or alkalinity of the medium. In unbuffered system, pH of the medium decreases from 10 to 3.4 during the reaction. Based on observed trends of reaction rate, energy, and entropy of activation, a mechanism for hypochlorite oxidation of starch is proposed.

### INTRODUCTION

Oxidation of starch with hypochlorite has been studied extensively by several workers.<sup>1-13</sup> McKillican and Purves<sup>9</sup> pointed out that 80-90% oxidation occurred at the hydroxymethyl group of the D-glucopyranose unit (GPU) of starch. Extensive studies by Whistler and co-workers have been carried out on oxidation of carbohydrates by hypochlorite and chlorine. Studies on oxidation of amylopectin with hypochlorite showed that the highest rate of reaction was obtained at pH 7.0, a little lower rate at pH 5.5 and 9.0, and the lowest at pH 11.0 and above.<sup>13</sup> The hydrolyzate of the oxidized amylopectin contained glyoxylic acid; the highest yield of the acid was obtained from the product oxidized at pH 7.0. A mechanism for the oxidation was advanced by the authors based on initial attack at C-2 or C-3 leading to the formation of a keto group, probably through an intermediate hypochlorite ester.

When wheat starch was oxidized with sodium hypochlorite and chlorine, the oxidation of various hydroxyls took place in the order C-1 > C-2 > C-3  $\gg$  C-6.<sup>14</sup> Recent studies<sup>15,16</sup> on the action of chlorine on starch, cellulose, and simple carbohydrate compounds in nonaqueous systems led to the postulation of a new mechanism of depolymerization called "chlorinolysis." In the chlorinolysis of glycosidic bonds, cleavage occurs between C-1 and the glycosidic oxygen, with formation of glycosyl chloride and elimination of the aglycone as the hypochlorite ester. The latter may undergo hydrolysis or dehydrochlorination to a carbonyl function while the glycosyl chloride may solvolyze to form a reducing terminal glucose unit.

Another mechanism based on attack by chlorinium ion at the glycosidic oxygen has also been advanced.<sup>17</sup>

Extensive kinetic studies together with analysis of functional groups formed during alkaline hypochlorite oxidation of starch have been reported by Lewin and co-workers.<sup>18,19</sup> The rate of reaction of granular starches with sodium hypochlorite in the pH range of 7.5 to 11.0 decreases with increasing pH up to 10, remaining practically constant thereafter at least upto 11.7 pH. The rate also increases as the initial oxidant concentration is decreased, the trend being less pronounced at pH 8 and 9 than at pH 10.

This paper reports the oxidation of maize starch with sodium hypochlorite under different conditions. A detailed kinetic approach is attempted to elucidate the reaction mechanism.

## EXPERIMENTAL

### Starch

Maize starch was purified by extractive means<sup>20</sup> using 80% methanol for 150 hr and with 0.1*N* hydrochloric acid for 3 hr. It had the following analysis: lipid, 0.23%; nitrogen 0.31%; and ash, 0.05%. The purified starch was sieved and the sample between 200 and 240 mesh B.S. sieves was used for experiments.

### Sodium Hypochlorite

Sodium hypochlorite solution was prepared by passing chlorine gas into ice-cooled sodium hydroxide solution. The hypochlorite solution had the following analysis: available chlorine, 140.5 gpl; sodium hydroxide, 65.1 gpl; chloride, 90.0 gpl; and chlorate, nil. The hypochlorite stock solution was stored in the dark at 0°–7°C.

The following buffer systems were used to maintain the pH at various hydrogen ion concentrations: sodium acetate + acetic acid (pH 4.0 and 5.5); disodium hydrogen phosphate + sodium dihydrogen phosphate (pH 7.0); sodium bicarbonate (pH 8.5); and sodium carbonate + sodium bicarbonate (pH 10.0).

### Oxidation of Starch

Oxidation of starch was carried out in a five-necked round-bottom flask (1000 ml) which was coated from the outside with a thick, black paint and placed in a water bath maintained at the desired temperature. The temperature fluctuations were less than  $\pm 0.05^\circ\text{C}$ . Glass and calomel electrodes were introduced in two necks, a stirrer and a thermometer in other two necks, while the fifth neck was employed for introducing reactants or for withdrawing aliquots of the reaction mixture. Buffer was added first, followed by dry starch. The contents were stirred with a speed of about 300 rpm and allowed to equilibrate at the desired temperature. Then, concentrated hypochlorite solution was added, all at a time. At

intervals, aliquots (0.5 ml) were withdrawn and diluted to about 50 times with ice-cold, distilled water. The unreacted sodium hypochlorite was determined by titration against sodium thiosulfate (0.01*N*).

### Calculations

The rate of reaction was calculated by the method of integration as well as by the graphic method,<sup>21,22,24</sup> using eqs. (1) and (2) for first-order and second-order rate constants, respectively:

$$k'_{\text{I}} = \frac{1}{t} \ln \frac{a}{a-x} \quad (1)$$

$$k'_{\text{II}} = \frac{1}{t} \left( \frac{1}{b-a} \right) \ln \frac{a(b-x)}{b(a-x)} \quad (2)$$

where  $k'_{\text{I}}$  is the first-order rate constant,  $k'_{\text{II}}$  is the second order rate constant,  $b$  is the initial oxidate concentration,  $a$  is the initial oxidant concentration,  $x$  is the consumption of oxidant after time  $t$ , and  $t$  is the time at which oxidant consumption was measured.

Energy of activation, entropy of activation, and free energy of activation were also calculated employing known relationships.<sup>24,26</sup>

## RESULTS AND DISCUSSION

The effects of buffer components and buffer concentration, concentration of hypochlorite, concentration of starch, pH, and temperature on the kinetics of heterogeneous oxidation of starch with hypochlorite were studied. The results of this study are discussed below.

### Buffer Type and Buffer Concentration

Table I shows the first-order rate constants for the hypochlorite oxidation of starch. The rate of reaction is considerably slower with the borate buffer than with the carbonate-bicarbonate buffer. The rate does not change appreciably with increase in borate ion concentration. Since borax is known to form complexes with hydroxyls of carbohydrates,<sup>28</sup> it is likely

TABLE I  
Effect of Buffer Concentration on Rate of Reaction at pH 10 and at 37°C Using 170 mmoles/l. Oxidant and 0.3085 moles/l. Starch<sup>a</sup>

Buffer	Concentration of buffer, <i>M</i>	Rate constant, min <sup>-1</sup>
Borate	0.101	0.0022
Borate	0.203	0.0019
Borate	0.500	0.0019
Borate	1.000	0.0014
Sodium carbonate-bicarbonate	1.000	0.0140

<sup>a</sup> Starch concentration is calculated on the basis of glucopyranose unit.

TABLE II  
Effect of Concentration of Sodium Carbonate-Bicarbonate Buffer at pH 10 and  
at 37°C on the Rate of Oxidant Consumption Using 112 mmoles/l.  
Available Chlorine and 0.617 mole/l. Starch

Buffer concentration, <i>M</i>	Rate constant, min <sup>-1</sup>
0.25	0.013
0.5	0.016
1.0	0.017

that some of the reactive sites in starch are deactivated by complex formation.

Table II shows the results obtained with the carbonate-bicarbonate system. At buffer concentrations lower than 0.25*M*, the pH drifted gradually towards the acid side as the reaction proceeded. When the concentration of the buffer was increased, the rate increased up to 0.5*M*, but did not change significantly thereafter. The increase in rate with buffer concentration is analogous to the change in ionic strength of the medium. Therefore, following the "swamping technique,"<sup>23</sup> 1*M* buffer concentration was used in all subsequent experiments.

#### Oxidant Concentration

First-order rate constants were determined at oxidant concentrations of 28 to 170 mmoles/l. and plotted against the respective oxidant concentration. The plots are shown in Figure 1. In contrast to normal behavior, the rate of reaction at pH 10 decreases with increasing oxidant concentra-

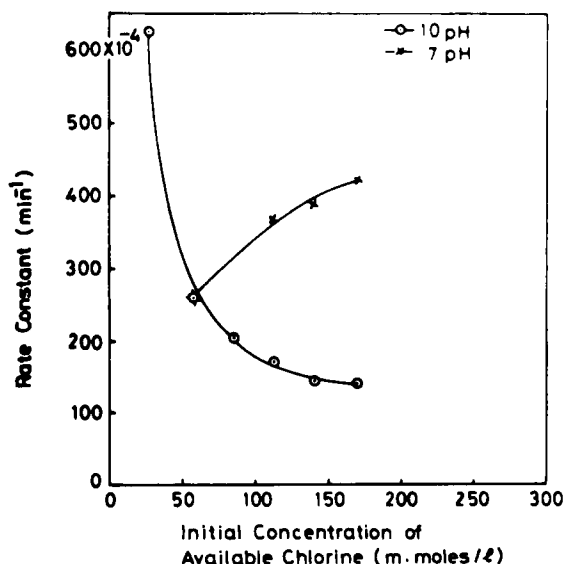


Fig. 1. Effect of initial oxidant concentration on first-order rate of oxidation reaction at pH 10 and 7 using 0.617 mole/l. starch at 37°C.

tion. At oxidant concentrations of 112 and 170 mmoles/l., the rate does not change appreciably. Such changes in rates with the oxidant concentrations have also been noticed by others.<sup>18,19</sup>

At pH 7.0, on the other hand, the rate constant increases with increasing oxidant concentration. Therefore, though the data may fit very well into the first-order plots, it is likely that some unknown factors also influence the rate of reaction.

### Starch Concentration

Table III shows the effect of starch concentration on the rate of oxidation. As the starch concentration is increased, the rate increases. The plot of starch concentration versus rate constant is a straight line which passes through the origin.

The second-order rate constants ( $k_{II}$ ) calculated for the reactions are also shown in Table III. For variations in starch concentration from 0.2 to 2.0 moles/l., the second-order rate constant practically remains the same. Significantly, these results ascertain that the component starch molecules take active part in determining the rate of reaction.

TABLE III  
Effect of Starch Concentration on Reaction Rates at  
37°C and pH 10 Using 170 mmoles/l. Oxidant

Starch concentration, moles/l.	Graphic rate constant	
	$k_I$ , min <sup>-1</sup>	$k_{II}$ , moles/l.-min
0.2056	0.0040	0.0310
0.3086	0.0075	0.0400
0.6172	0.0170	0.0290
1.0284	0.0315	0.0340
1.2340	0.0375	0.0330
1.5430	0.0510	0.0350
2.0560	0.0690	0.0350

### Hydrogen Ion Concentration (pH)

The rates of oxidation of starch with hypochlorite were also measured at pH 8.5, 7.0, 5.5, and 4.0 using four levels of oxidant concentration. Figure 2 shows the plots of first-order rate constants versus pH at various oxidant concentrations. The rates at all the oxidant concentrations are highest at 7.0 pH and decrease with increasing acid strength of the medium. Similarly, the rates also decrease with increasing alkalinity of the medium. This characteristic dependence of rate on pH has been observed earlier for starch, cellulose, and other carbohydrates by various workers<sup>30-34</sup> and has been attributed to changes in the oxidizing species. However, the retardation of rate could also be due to presence of acid and alkali. This is discussed in detail later on.

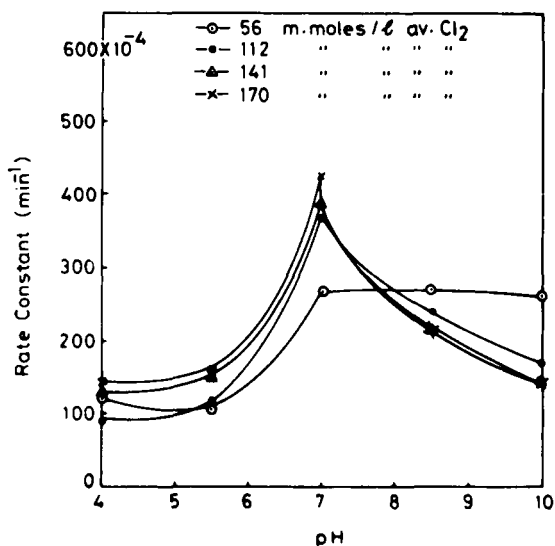


Fig. 2. Effect of pH on rate of oxidation of starch at various initial oxidant concentrations.

### Temperature

Table IV shows rate data obtained at temperatures of 27°, 37°, and 47°C and at different pH levels. Table V shows the data on energy of activation, free energy of activation, and entropy of activation. It is evident from Table IV that, irrespective of temperature, the rate of reaction is highest at 7 pH and decreases with increasing acidity or alkalinity of the medium.

Examination of Table V shows that, whereas at different pH the energy of activation and entropy of activation are altered considerably, the free energy of activation remains practically constant. It is noteworthy that, although the maximum rate is at pH 7, minimum values for the energy of activation and the entropy of activation occur at pH 5.5. The graph of  $\Delta E^*$  versus  $\Delta S^*$  for values at different pH levels is a straight line, suggesting that the decrease in the energy of activation is compensated by the

TABLE IV  
Effect of pH and Temperature on Graphic Rate Constant of Oxidation of Starch with 112 mmoles/l. Hypochlorite and 0.6172 moles/l. Starch

pH	Rate constant, $\text{min}^{-1}$		
	27°C	37°C	47°C
4.0	0.0054	0.0087	0.0306
5.5	0.0048	0.0117	0.0274
7.0	0.0132	0.0370	0.0890
8.5	0.0078	0.0240	0.0600
10.0	0.0045	0.0170	0.0562

TABLE V  
Effect of pH on Energy of Activation, Entropy of Activation, and Free Energy of Activation at 112 mmoles/l. Oxidant and 0.6172 moles/l. Starch

pH	$\Delta E^*$ , kcal	$\Delta G^*$ , kcal	$\Delta S^*$ , E.U.
4.0	23.4	23.7	-0.95
5.5	15.9	23.5	-24.50
7.0	17.6	22.8	-16.77
8.5	18.4	23.0	-14.94
10.0	23.7	23.2	-0.32

corresponding decrease in the entropy of activation. Such a trend indicates that energy of activation and entropy of activation both influence considerably the overall rate of reaction. The activated complex may give reaction products easily by way of low energy barriers but the frequency of formation of such a complex may be brought down by corresponding greater requirements of orientation, alignment, or association of the reactants.

Therefore, overall reaction may not show the trend of higher rates at lower energy of activation. This is particularly true at pH 5.5. At this pH, entropy of activation (-24.40 E.U.) is lowest, indicating the formation of a highly ordered activated complex. Consequently, frequency of formation of such complexes will be reduced very much. On these considerations, the energy of activation is lowest at pH 5.5, but the rate is not highest at this pH. At pH 7.0, the entropy of activation is -16.77 E.U., suggesting a considerably less ordered activated complex than that at pH 5.5. Since the energy of activation at pH 7.0 is only 1.7 kcal greater than that at pH 5.5, the rate is highest at pH 7.0.

### Mechanism

The complex nature of hypochlorite oxidation has been attributed to various reacting species in solution at different pH.<sup>35</sup> Under alkaline conditions, mainly  $\text{OCl}^-$ ; near neutral pH, undissociated  $\text{HOCl}$  and  $\text{OCl}^-$ ; and at pH 5.5 and 4.0, undissociated  $\text{HOCl}$  are predominantly present. The chlorine molecules are formed increasingly as the acidity of the medium increases. The chlorinium ion has also been suggested as one of the oxidizing species.<sup>17</sup> Starch is oxidized with one or more of these species at sites C-1, C-2, C-3, and C-6 of GPU. At these sites, the oxygen atom remains intact, whereas the hydrogen attached to the carbon atom is removed thus converting hydroxylic functions into ketonic or carboxylic groups. This transformation, which increases the polarity of the starch molecule, is expected to decrease the entropy of activation.

Component starch molecules would display different structural changes under acid and alkaline conditions. Formation of soda starch under alkaline conditions and protonation and/or hydrolysis under acid condi-

TABLE VI  
Change in pH During Unbuffered Hypochlorite Oxidation of Starch at 37°C  
and 0.3085 mole/l. Starch

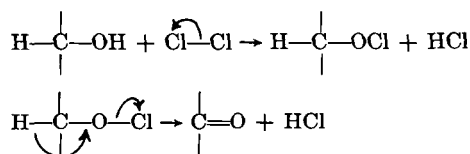
Time, min	pH	Oxidant concentration, mmoles/l.
0.0	10.00	167.9
2.5	9.20	160.4
5.0	8.99	157.0
10.0	8.60	151.0
20.0	8.30	145.2
30.0	8.00	136.3
45.0	7.60	109.7
60.0	7.00	75.5
75.0	6.20	54.0
90.0	5.50	48.5
120.0	4.20	40.5
150.0	3.90	35.7
180.0	3.63	30.4
240.0	3.42	23.6

tions are well known. Therefore, the structural changes in starch molecule with change in pH of the reaction medium should also affect the rate.

The oxidation reaction is invariably accompanied by the liberation of acid as a by-product. For example, an unbuffered system at pH 10.0 attained a pH of 3.4 after almost all the oxidant was consumed. Table VI shows data regarding change in pH with time.

A mechanism based on the transfer of two protons is postulated hereunder to explain the above findings. According to this mechanism, one proton is transferred from the —OH group, whereas the other is transferred from the  $\begin{array}{c} | \\ \text{H}-\text{C} \\ | \end{array}$  function. Depending on reaction conditions, any one of the proton transfers may be the rate-determining step.

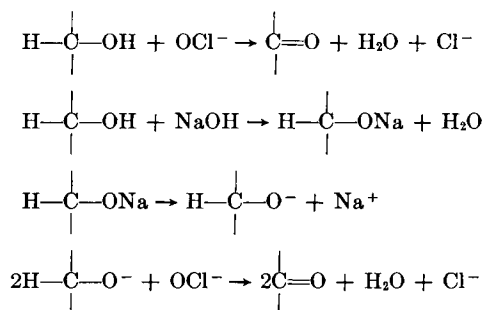
Scheme I— Acidic Conditions:



When the reaction medium is highly acidic, hypochlorite is rapidly converted into chlorine molecule which subsequently reacts with starch hydroxyls, as shown in scheme I. Formation of acidic products in acid conditions would be relatively slow. Protonation of hydroxyls with increasing acidity is also possible. Therefore, the rate of reaction would be increasingly lower with increasing acidity of the medium. Such a trend is commonly observed between pH 4 and 7.

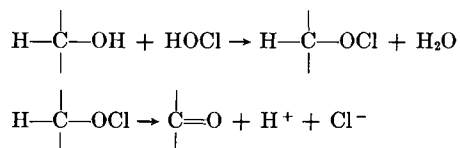


Scheme II—Alkaline Conditions:



Under alkaline conditions, the rate of formation of soda starch predominates over starch-hypochalite ester formation. Soda starch would dissociate leaving a negative charge on the starch molecule. Evidently, the reaction between  $\text{OCl}^-$  anion and starch- $\text{O}^-$  will be relatively very slow. Under slightly alkaline conditions, the rate would be relatively higher because a sizeable portion of starch molecules would still remain neutral. Observed rate of reaction shows the expected trend.

Scheme III—Neutral Conditions:



Under neutral conditions, both the reactants are essentially neutral, but aqueous medium affords enough polarity to promote formation of by-products. At the cost of undissociated weak acid, water and strong acid are formed as by-products. Acid is readily removed by buffer components to maintain a neutral pH. Therefore, the observed rate of reaction is highest at pH 7.0.

The changes in the entropy of activation and energy of activation at various pH levels also support the proposed mechanisms. The formation of  $\text{H}^+$  in aqueous medium takes place with lowering of the entropy of activation.<sup>25</sup> Strong orientation of water molecules around the proton leaving the starch molecules during the activation step requires reduction of entropy of activation. Therefore, in the aqueous hypochlorite oxidations, the entropy of activation values are negative. At near-neutral or at slightly acidic pH, polar products such as  $\text{H}^+$  and  $\text{Cl}^-$  and ketonic groups are formed from the neutral reactants such as undissociated  $\text{HOCl}$  and starch hydroxyl. The interaction between the leaving proton and neutral water molecules is also highest. Therefore, the entropy of activation is the least. The energy of activation is also least at these pH levels, because there are hardly any charge barriers preventing free access of reactants to each other for the formation of the activated transition state complex.

Under alkaline conditions, base-catalyzed elimination of proton from the activated complex actually decreases  $\text{OH}^-$  and  $\text{H}^+$  ions, with formation of neutral  $\text{H}_2\text{O}$ . Therefore, removal of charged species and formation of neutral species in solution would change orientation of solvent molecules. Relatively, the negative entropy of activation accompanying formation of  $\text{H}^+$  in alkaline conditions is not as high as that observed in the acidic condition. The energy of activation is higher under alkaline conditions than that at neutral pH, because the interaction between starch— $\text{O}^-$  and  $\text{OCl}^-$  needs greater energy to overcome charge barriers for the formation of the activated complex in alkaline medium.

Under acidic conditions, removal of proton is inhibited. Since the system already contains a large concentration of  $\text{H}^+$ , additional  $\text{H}^+$  ions formed during reaction do not materially change the orientation pattern of solvent molecules. Therefore, the entropy is not lowered to the same extent as at neutral pH. The energy of activation is also expected to be higher in acidic medium than that in the neutral medium, because the barriers for the formation of the polar activated complex would be greater in the acidic pH than in the neutral pH. The first proton transfer from the hydroxyl group may take place rapidly up to about pH 4.0, because OH bonds are weakly acidic and can dissociate up to pH 2.5, which is the isoelectric point of hydroxyl-containing polymers like cellulose. However, the

second proton transfer from  $\begin{array}{c} | \\ \text{C}-\text{H} \\ | \end{array}$  would require greater energy because the bond is stronger than the OH bond. Unlike alkaline conditions, there is no base-catalyzed elimination of  $\text{H}^+$  from C—H. Therefore, the activation energy for the removal of second proton is high under acidic conditions.

### CONCLUSIONS

The kinetics of hypochlorite oxidation of starch fit into a first-order reaction. However, when the initial oxidant concentration is increased, the rate constant increases at pH 7.0 and decreases at pH 10.0. The first-order rate constant also increases linearly with increase in starch concentration. As with other carbohydrates, the rate of reaction is highest at pH 7.0. Above and below this pH, the rate decreases with increasing alkalinity or acidity of the medium. In an unbuffered system, the pH of the reaction medium changes from 10 to 3.4 during the course of oxidation, suggesting liberation of acidic by-products. From the results obtained for rate, energy, and entropy of activation, a mechanism for the hypochlorite oxidation of starch has been proposed. The mechanism postulates two successive

proton transfers, one from —OH and the other from  $\begin{array}{c} | \\ -\text{C}-\text{H} \\ | \end{array}$  of the glucopyranose unit. The presence of a high concentration of protons in acidic medium and repulsion between two anions in alkaline medium explain the rate retardations observed under acidic and alkaline conditions, respectively.

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