Kinetics and Mechanism of Hypochlorite Oxidation of Holocellulose from Eucalyptus Hybrid in the pH Range 2-10

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In the present study, the kinetics and mechanism of sodium hypochlorite oxidation of holocellulose isolated from Eucalyptus hybrid in the pH range 2-10 has been reported.

Kinetic plots were obtained by periodically citrating aliquotes iodometrically. The reaction was characterized by an initial rapid oxidation, attributed to the presence of lignin as impurity followed by a slow reaction, the oxidation of holocellulose.

In the later slow reaction, the rate of consumption of available chlorine follows a second order rate equation :

$$1/C_t = 1/C_o + k_2 t$$

The rate of oxidation was increased nearly two times for every 10° rise of temperatures. Energy parameters of the reaction have also been reported.

The reaction is faster in the acidic medium (maximum at pH 2). This may be ascribed to the change in reacting species as well as due to the presence of hemicelluloses in holocellulose.

The oxidation in this pH range is governed by the rate law equation :

$$-\frac{d[Cl_2]}{dt} = k_2[Cl_2]^2$$

The reaction has been explained on the basis of hydride transfer or proton transfer mechanism.

Introduction

Holocellulose is a term used to refer the total carbohydrate fraction of plant raw material, which is left after the lignin is removed. It accounts for roughly three fourths of the wood substance, and contains cellulose and hemicelluloses. It is this fraction, that interests the chemists concerned with the pulp industries.

The presence of hemicelluloses is essential for paper grade pulp, as they contribute to the strength and increase the yield. On the other hand, a total absence of hemicelluloses is desired, for rayon grade pulp. For producing this pulp, acid or alkali hydrolysis is adopted to remove lignin.

The presence of multiple easily oxidable groups makes a carbohydrate molecule particularly susceptible to oxidation. The carbonyl groups (either free or in hemiacetal form), as well as primary and secondary alcoholic groups present vulnerable points of attack for an oxidising agent and the process is often complicated by ruptures of bonds between C—C. Moreover, oxidations leading to progressive lowering of the solution pH is likely to bring about additional hydrolytic cleavage of glycosidic linkage of oligo-and polysaecharides.

Large scale plantations of eucalyptus hybrid are being raised throughout the length and breadth of the country to meet the growing needs of both paper and rayon grade pulp.

The work described here, has been carried out in order to throw some light on the reaction parameters to obtain the desired end product. An effort has been made to find a mechanism which will account for the kinetics of these reactions.

A survey of literature reveals that very little work has been carried out on kinetics and mechanism of oxidation of holocellulose from eucalyptus hybrid with hypochlorite at varying pH values.

It has been reported by Tokumi Koshizawa[1] that the action of sodium hypochlorite is preferential on hemicelluloses to cellulose. Okubo K and co-workers[2] found that during the oxidation of *Pinus densiflora* holecellulose with calcium hypochlorite, hemicellulose suffered more and faster degradation than cellulose. Recently Guha and co-workers[3] observed that when bamboo

(Dendrocalamus strictus) holocellulose was treated with hypochlorite, at varying pH values, the rate of oxidation was maximum in the acidic medium and was highest at pH 4.

Exprimental Method

Holocelluloses was prepared from extractive free eucalyptus hybrid dust (60-80 mesh) by the chlorite method of Wise and co-workers[4].

Analysis of holocellulose was carried out according to Tappi Standard methods.

Solution of hypochlorite was prepared by passing a slow stream of chlorine gas into a well cooled solution of 2 N sodium hydroxide, until the increase in weight indicated that about 50 g. per litre of chlorine was absorbed. This solution was stored in a dark bottle at 3°C. The solutions for oxidation were prepared from it by suitable dilutions.

It was established in the preliminary experiments, that under the conditions employed in this investigation, sodium hypochlorite solution was stable and that the substrate was always present in sufficient excess so that the rate of reaction, with respect to hypochlorite concentration, expressed as available chlorine, could be legitimately established by studying the change occurred in the chlorine concentration with time alone.

Determination of the rate of oxidation

The reaction was studied in 500 ml. five necked pyrex glass round bottom flask (Fig. 1). A thermostatic bath with a temperature variation of ±0.1°C was used for maintaining the temperature. To prepare the reaction mixture sodium hypochlorite solution and 0.5 N hydrochloric acid or 0.5 N sodium hydroxide solution were mixed in such a proportion so that a solution of desired pH and $[NaOCl]_o$ concentration was obtained. A weighed amount of holocellulose was transferred to the reaction vessel. Calculated quantities of distilled water were added so that the total volume of the substrate suspension after the addition of hypochlorite reaction mixture becomes equal to 200 ml. pH during the reaction was kept constant by addition of 0.5 N sodium hydroxide solution from, burette fixed at 'b' (Fig. 1). Two electrodes of the pH meter were inserted through E_1, E_2, the two necks of the reaction vessel and were sealed. Mercury sealed glass stirrer was fitted in the central neck. Rubber stoppered Neck A was used for the addition of hypochlorite solution and for the removal of aliquotes for estimation of residual chlorine.

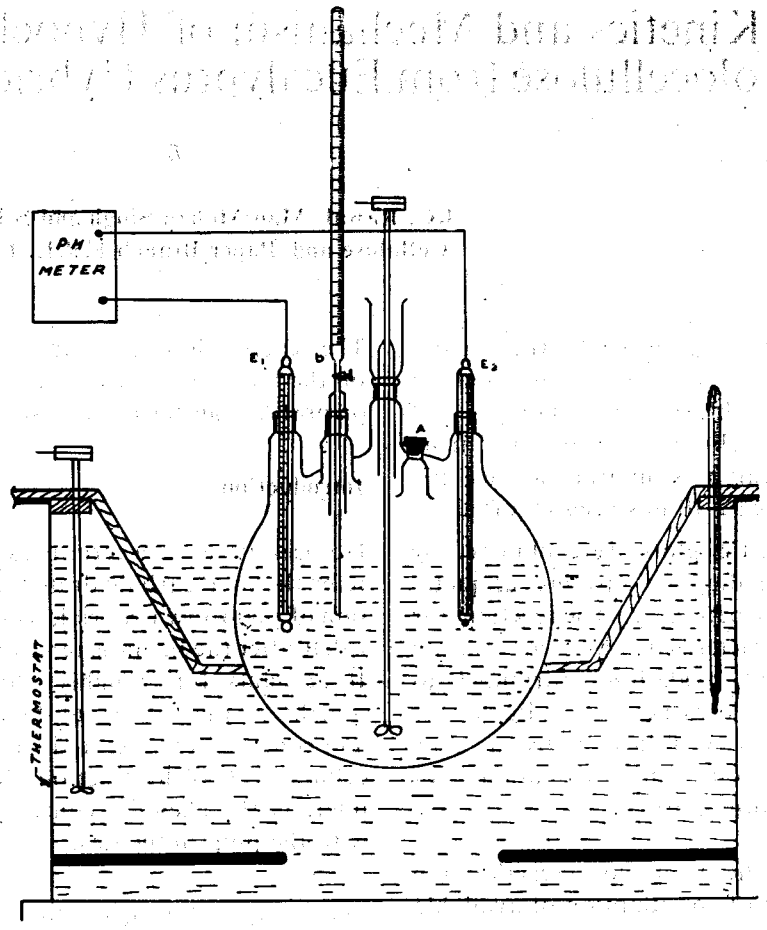

FIG. 1. REACTION APPARATUS

The progress of the reaction was followed by estimating residual available chlorine iodometrically at different intervals of time.

Chlorate formation was evaluated by standard procedures[5] in

these reactions at periodic intervals.

Results & Discussions

1. Analysis of holocellulose

The results of holocellulose analysis are given in Table 1.

TABLE 1

Analysis of holocellulose

Alpha cellulose	= 64.6%
Hemi cellulose	= 34.0%
Klason lignin	= 1.0%

These results indicate that holocellulose is mainly comprised of alpha cellulose and hemicelluloses. Some of the lignin is present as impurity.

2. Kinetics of oxidation of holocellulose in the pH range of 2-10

The oxidation of holocellulose with hypochlorite was marked by an initial rapid reaction, which took a few minutes (5-10 min.) followed by a slow reaction (Figs. 2, 3).

The behaviour of oxidation reaction being rapid at the initial stages may be ascribed to the presence of lignin as impurity, which oxidises at a much faster rate than the holocellulose. The subsequent slower rate of oxidation corresponds to the oxidation of holocellulose and followed a second order kinetics with respect to oxidant concentration, when expressed as available chlorine. In general all the plots obtained at all pH values in this series (Figs. 4-6) were found to be best fitted by a linear relationship.

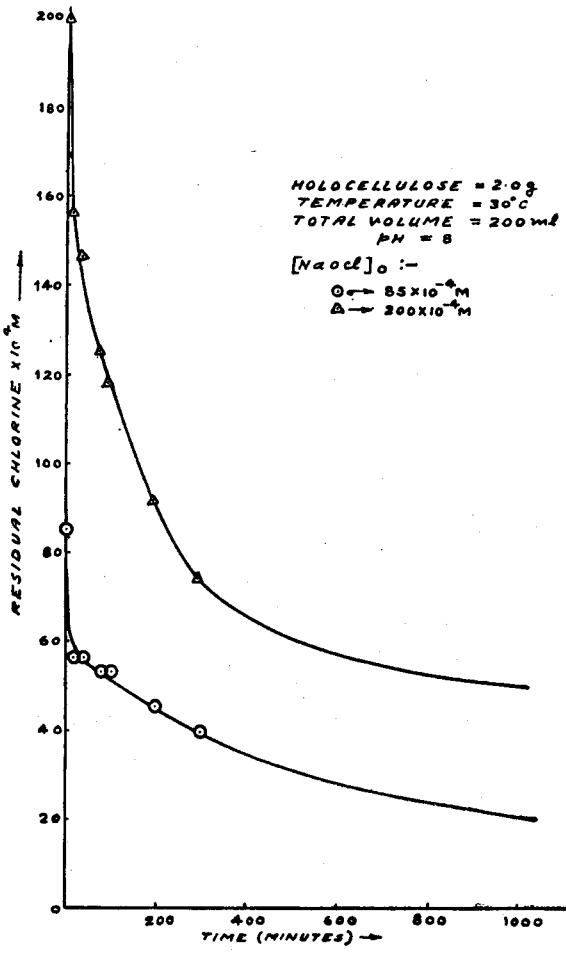

FIG.2. CONCENTRATION-TIME CURVES

$1/C_t = 1/C_o + k_2 t$

Where C_t and C_o are the concentration of available chlorine at time 't' and initially, k_2 being the rate constant. For the purpose of comparing the rate of oxidation under various conditions, the values of 'k'_2 were calculated from the slope of the straight line.

Dependence of the rate of oxidation on initial concentration of hypochlorite

The rate of oxidation was found to decrease linearly with the increase in the initial concentration of hypochlorite, when expressed in terms of available chlorine (Fig. 7).

This shows that the rate of oxidation is dependent not only on the initial concentration of any single species present in equilibrium,

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^-$$
$$HOCl \rightleftharpoons H^+ + OCl^-$$

but on some combination of species. (The possibility of these

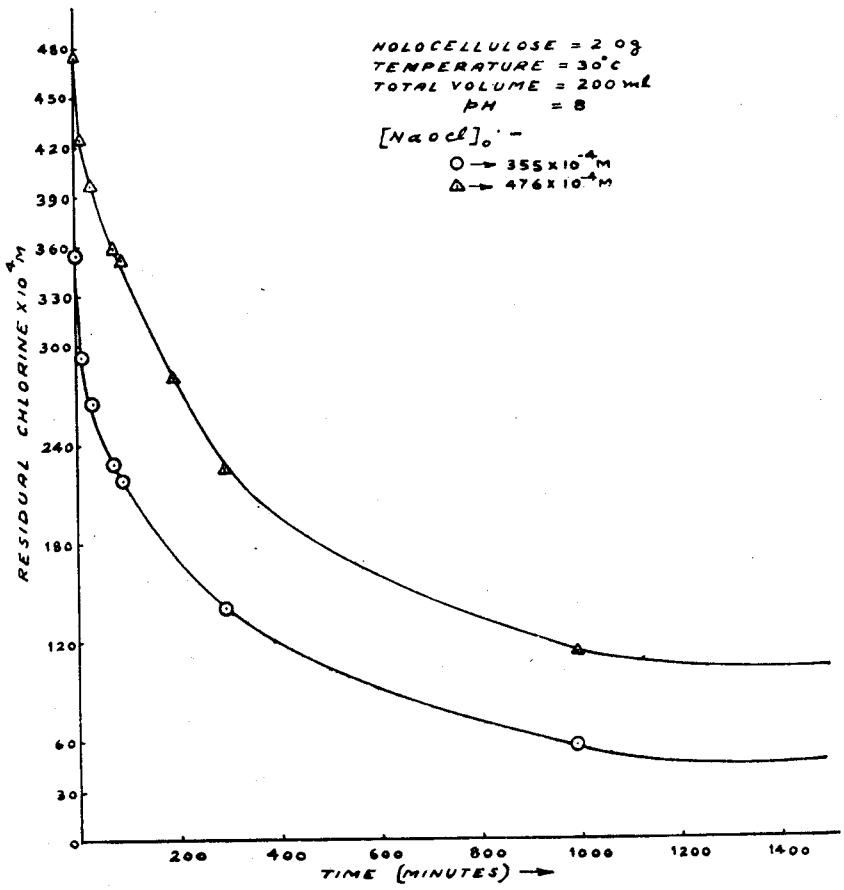

FIG 3 CONCENTRATION-TIME CURVES

various reacting species had been discussed while postualating the probable mechanism to account for the kinetics of this reaction.)

Dependence of the rate of oxidation on the concentration of holocellulose

It has been found that the rate of oxidation increases with increasing concentration of holocellulose, and is proportional to the square of holocellulose concentration (Fig. 8).

Dependence of the rate of oxidation on temperature and energy parameters of the reaction

The effect of temperature on the rate of oxidation and the values of the energy parameters of the reaction are recorded in Table 2.

Perusal of the data recorded in this table showed, that the oxidation rate increased nearly two times with every 10°C rise of temp. The temperature coefficient being 2.

The values of the free activation energy showed that indices were practically the same, under different reaction conditions. This was an indication of tendency for heat and entropies to compensate one another leading to only a slight change in the free activation energy.

Guha and co-workers[6], have also reported compensation effect during their studies on hypochlorite oxidation of bamboo hemicellulose.

When the logarithms of rate constants were plotted against the reciprocals of the respective temperature (°K) straight lines were obtained (Fig. 9), establishing thereby the validity of

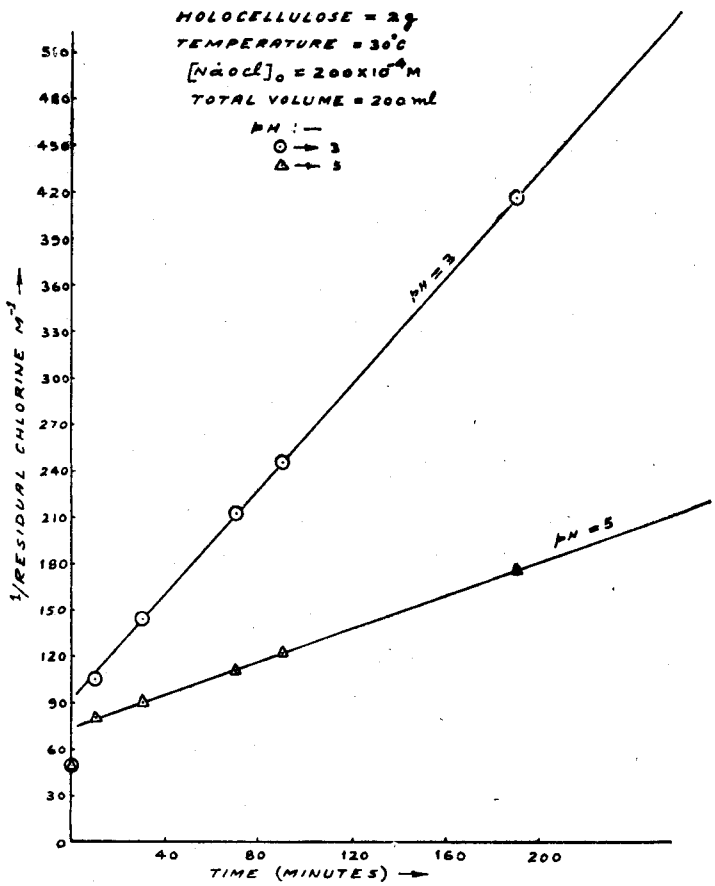

FIG 4 EFFECT OF pH

TABLE 2

Holocellulose = 2g pH ≠ 8 Total volume = 200 ml.

$[NaOCl]_0$ $x\ 10^{-4}M$ 1	Temp. °C 2	Rate Const. $IM^{-1}\ Min^{-1}$ 3	Temp. Coeff. 4	$\triangle E$ K Cals $Mole^{-1}$ 5	$A\ x\ 10^{-12}$ $Sec.^{-1}$ 6	$\triangle F\%$ K Cals $Mole^{-1}$ 7	$\triangle S\%$ E.U. 8
200	20	0.11			2.68	21.45	—28.53
200	30	0.25	2.27	14.45	2.77	21.72	—28.00
			1.71	11.86			
200	50	0.87			2.96	22.28	—28.35
			1.90	13.15	2.87	21.82	—28.29
				13.33 (graphically)			
275	20	0.075			2.50	21.70	—29.98
			2.00	12.18			
275	30	0.150			2.49	22.00	—30.86
			2.00	13.46			
275	50	0.600			2.76	22.61	—30.10
			2.00	12.82	2.62	22.10	—30.32
				12.75 (graphically)			

1	2	3	4	5	6	7	8
385	20	0.05	2.00	12.18	2.46	22.38	—30.78
385	30	0.10	2.00	13.46	2.54	22.53	—30.96
385	50	0.40			2.71	22.80	—30.90
			2.00	12.82 12.56 (graphically)	2.50	22.57	—30.80

Arrhenius equation relating temperature with rate constant.

Dependence of the rate of oxidation on the pH

The rate of oxidation was found to be highly dependent on pH of the reacting system. It was observed (Fig. 10) that the rate of oxidation was maxi-

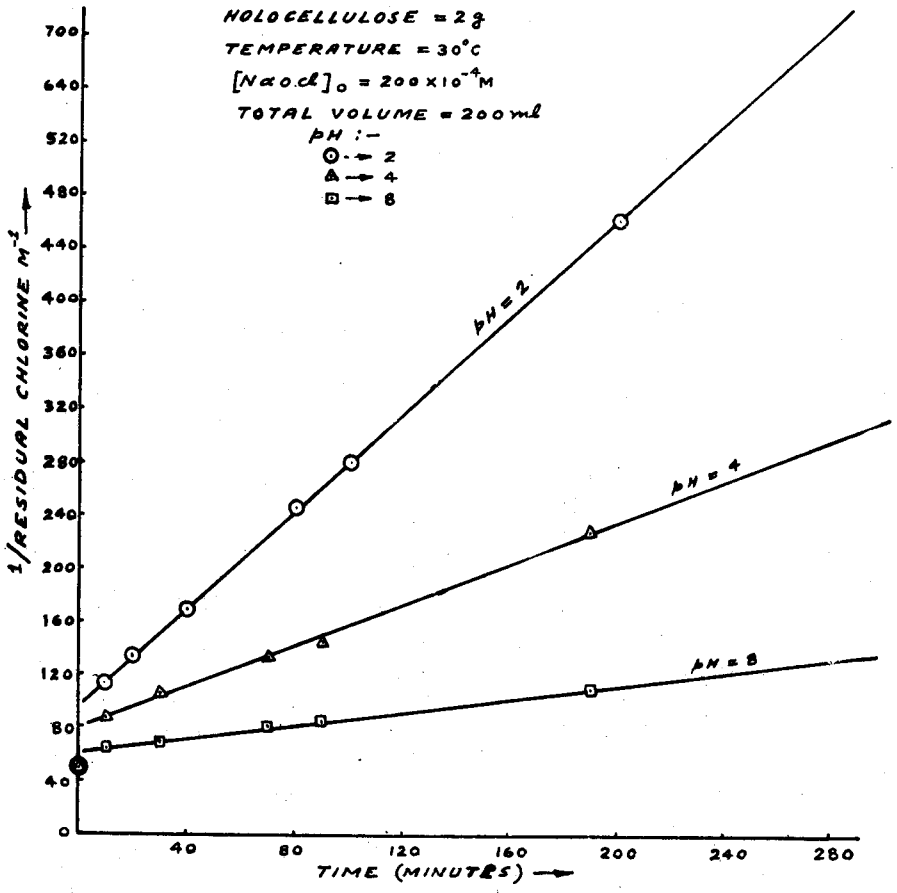

FIG. 5. EFFECT OF pH

mum at pH 2. It decreased sharply between pH 3 and 4. Beyond this pH, the rate decreased gradually with increase in pH of the system. This variation in oxidation rate may be due to the changes occurring in the composition of hypochlorite and the reacting species, with change in pH of the system. The reaction being much faster in the acidic medium (pH 2-4) may be attributed to the presence of hemicellulose in holocellulose which react at a much faster rate than the remainder[1-3] (cellulose) in this pH range.

The variation noticed in the oxidation rate cannot be attributed to the self decomposition of hypochlorite to chlorite, since no chlorate was found to be formed during the oxidation process.

This behaviour shows that a complex set of reaction mechanism is involved.

Rate Law

Since it is not possible to express the concentration of holocellulose molarity, it is only appropriate to write the rate of decrease of the concentration of oxidant (as available chlorine) in relation to its own concentration.

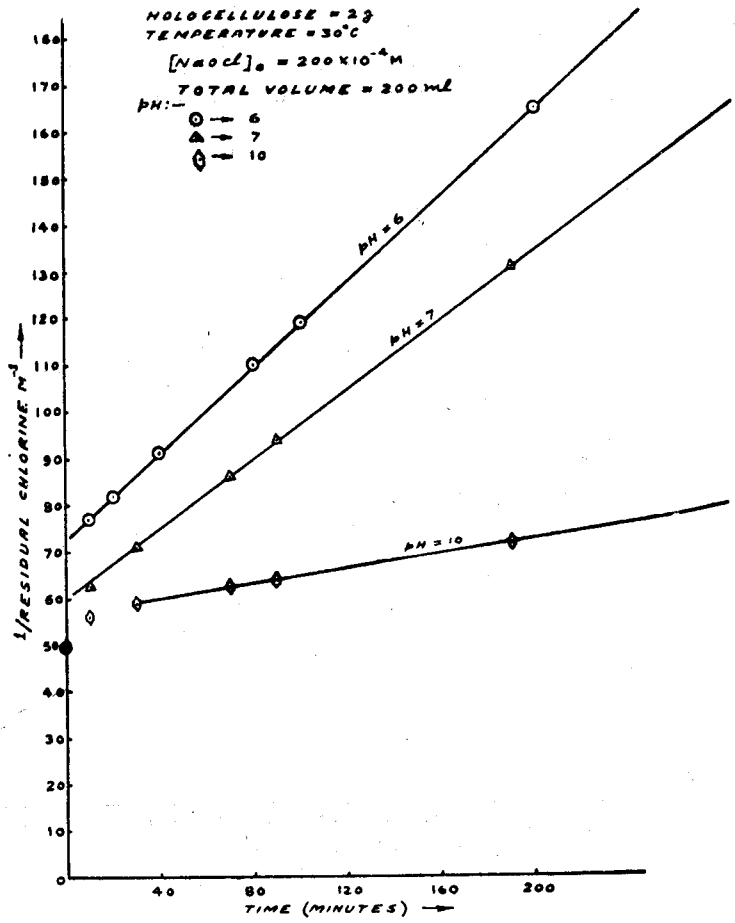

FIG 6 EFFECT OF pH

The data recorded in this investigation shows that :

$$-\frac{d[Cl_2]}{dt} = k_2 [Cl_2]^2$$

where

$[Cl_2]$ is the concentration of available chlorine estimated iodometrically.

Reaction mechanism

The manner in which the rate of oxidation of holocellulose is changing with pH suggests that a complex set of reaction machanism is involved. Therefore a clear cut kinetic treatment of the results is difficult. However, because of the technical importance of oxidation of wood carbohydrates by compounds native in chlorine, it is of value to throw some light on the main reacting species present and the reaction mechanism involved based on our experimental data recorded and available published literature.

Considerable evidence has been presented that the chlorine

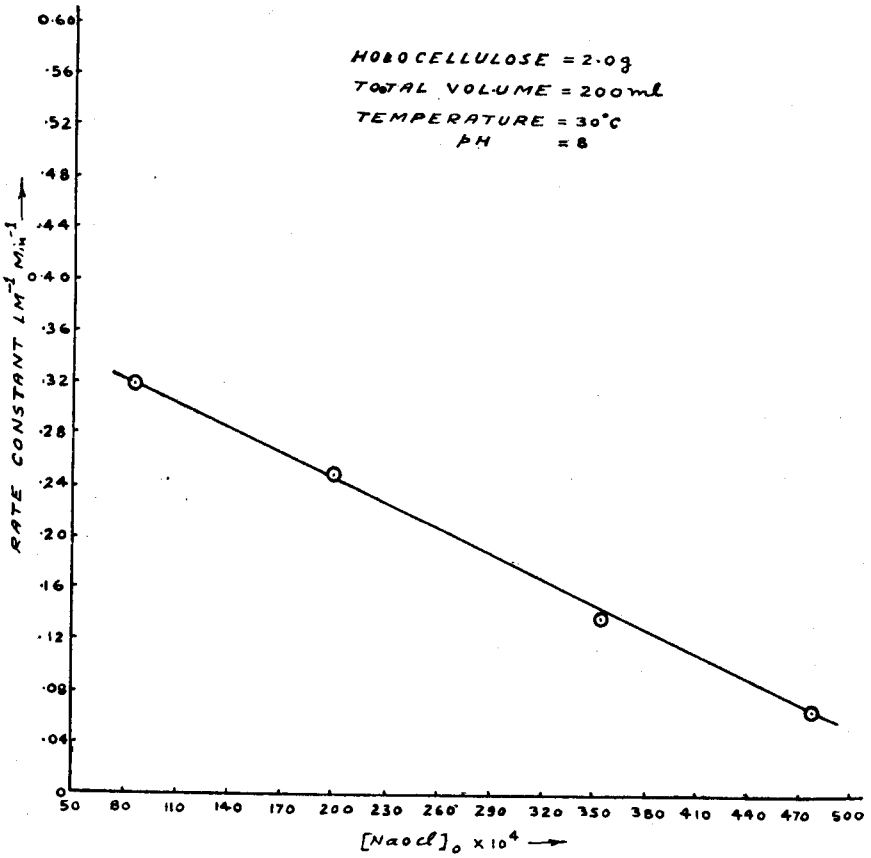

FIG.7. RATE CONSTANT VS $[NaOCl]_0$

oxidation of various carbohydrates in acid aqueous solution takes place by a combination of both radical and ionic reaction[7,8]. Both the ionic and radical components of the oxidation are composed of a number of different reactions. The rate of these reactions depend on pH and reactant concentrations in different ways as is indicated for instance by the fact that the product mixture changes composition with pH.

The hydrolysis of chlorine in water is represented by the equation as has already been described.

$$Cl_2 + H_2 \rightleftharpoons OHOCl + H^+ + Cl^-$$

The hydrolysis is so rapid that Cl_2 and HOCl can be considered to be in equilibrium throughout the run[9]. The best fit rate law equation derived by Theander and co-workers[10] suggested that chlorine mono-

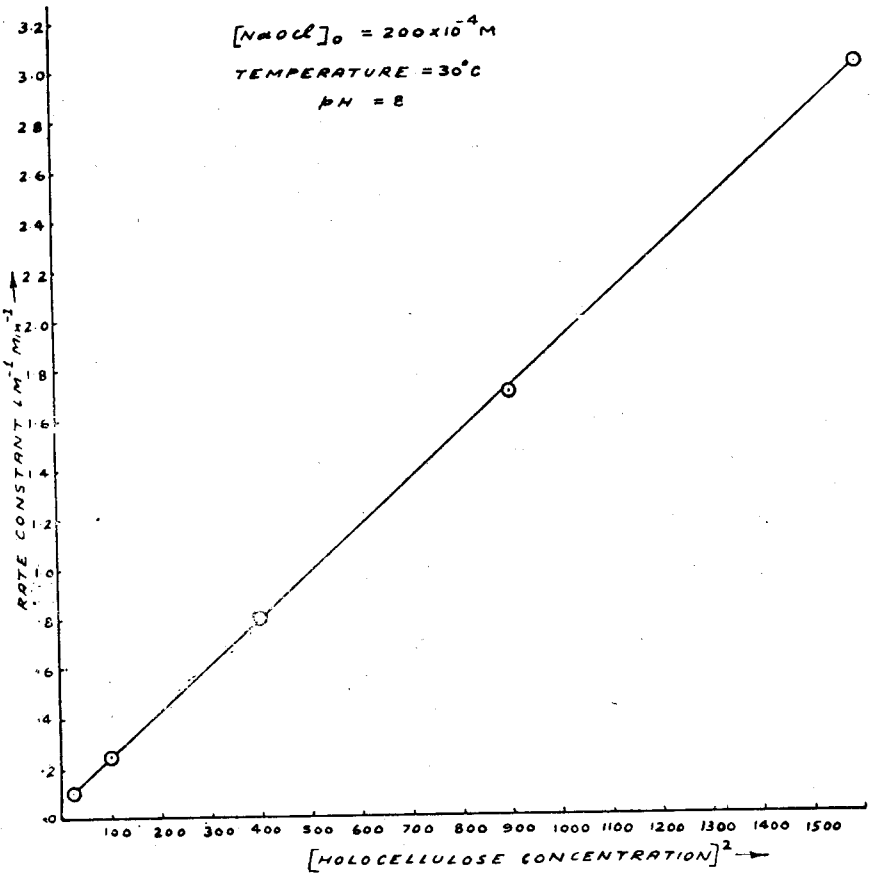

FIG 8 RATE CONSTANT VS [HOLOCELLULOSE CONCENTRATION]²

xide can be considered as a possible reactant and might be a more effective oxidant than HOCl inspite of its lower concentration. However, their suggestion of participation of Cl_2O in the oxidation is tentative especially when the rate of halogen oxidation of even simple alcohols depends on pH in a way which is difficult to explain[11].

Whistler and co-workers[12] have recently studied the chlorine oxidation of acetylated methyl β-D-glucupyranoside in non-equeous solution. They suggested that the oxidation involved a cleavage of the glycosidic bond to give glucose and hypochlorite ester of methanol as the main reaction products.

Bromine oxidation of simple alcohols and ethers has been suggested to take place by hydride transfer [13,14] or proton transfer both of which involves the formation of a resonance

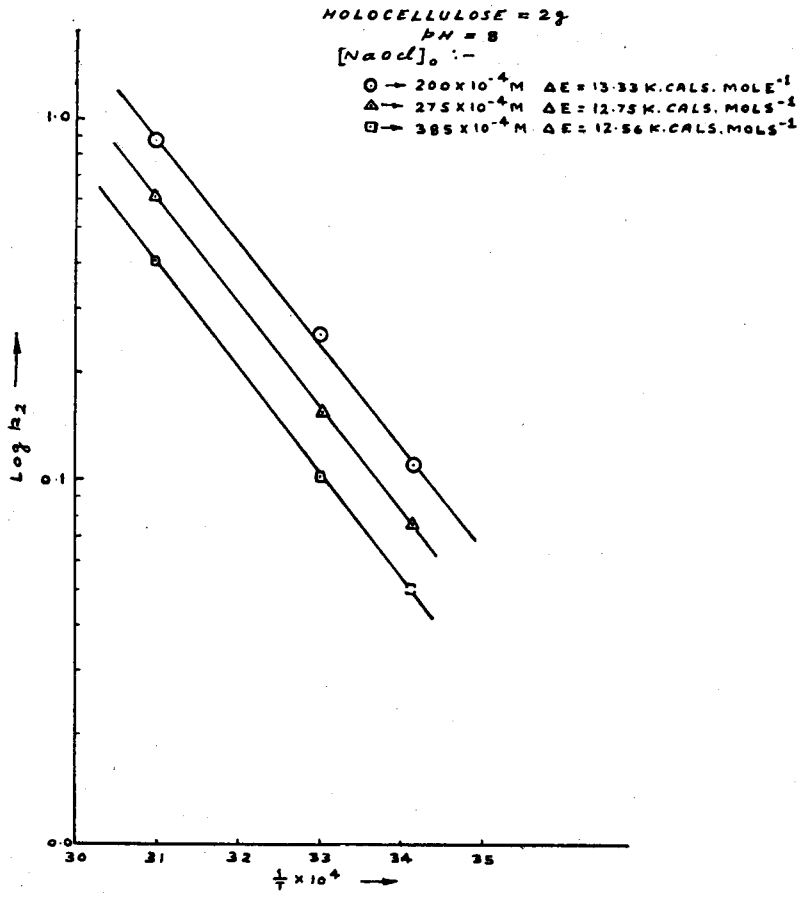

FIG. 9 ARRHENIUS PLOT FOR THE OXIDATION OF HOLOCELLULOSE

established carbonium oxonium ion intermidiate[15]. Theander and co-workers[10] have also suggested similar process for oxidation of methyl β-D glucopyranoside by chlorine. It seems reasonable, therefore to suggest the chlorine oxidation of holocellulose also occurs analogously.

Besides the hydride or proton transfer machanism, HOCl and Cl_2O may estrify the hydroxyl groups to hypochlorite ester groups which subsequently give carbonyl groups,

$$>CHOH + HOCl \rightleftharpoons CHOCl + H_2O$$

$$>CHOH + Cl_2O \rightleftharpoons CHOCl + HOCl$$

$$>CHOCl \longrightarrow CO + HCl.$$

Conclusion

Kinetic investigations on the oxidation of holocellulose reveal that due to the oxidation of hemicellulose present in holocellulose, and changes in hypochloritesp ecies, the reaction is faster in the lower pH range (pH 2-4), than in the alkaline pH range. For the retention of hemicelluloses the reaction should be carried in strongly alkaline medium. Whereas for their complete removal the reaction should be carried out in acedic medium at about pH 2.

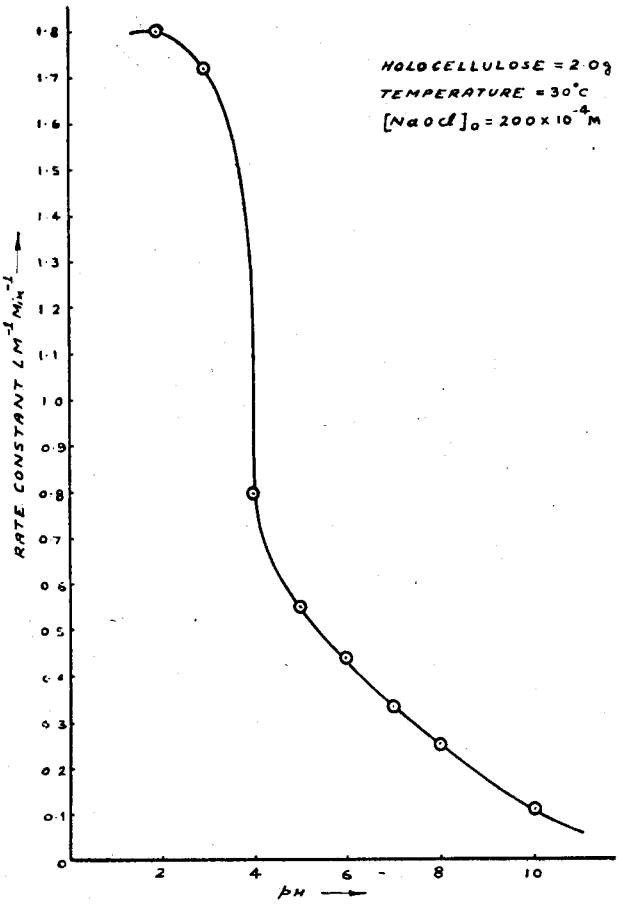

FIG. 10 RATE CONSTANT VS pH

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