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Degradation of Cellulose by Alkaline Oxidation

O.P.Golova and N.I.Nosova

Investigations on the alkaline and oxidative-alkaline degradation of cellulose by molecular oxygen are reviewed, and the reaction mechanisms are surveyed. The effect of the supermolecular structure of cellulose on the rates of these processes is examined. A list of 136 references is included.

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I. INTRODUCTION

The problem of the oxidative degradation of cellulose embraces a very wide range of scientific and practical questions—oxidising reactions, the effect of chemical and supermolecular structure on the oxidation of cellulose, the changes in chemical, physical, and mechanical properties of cellulose produced by oxidants, etc. The present Review discusses aspects of the alkaline and oxidative–alkaline degradation of cellulose and the mechanisms of the reactions involved.

II. ALKALINE DEGRADATION OF CELLULOSE AND OXIDISED CELLULOSES

The oxidation of cellulose by molecular oxygen in alkaline media is a very complicated process, involving genuine oxidation reactions and also reactions undergone by the initial cellulose and its oxidation products under the influence of alkalis. In order to obtain a better understanding of this complicated question, it is advisable firstly to consider the reactions occurring during the alkaline degradation of cellulose and oxidised cellulose.

The reactions involved in the degradation of carbohydrates under the influence of alkalis are also very complicated, and have been discussed in detail in several review papers and monographs [1–8]. We therefore give only the principal experimental results together with modern views on the mechanism of the reactions involved.

1. Alkaline Degradation of Cellulose

The main processes occurring in the alkaline degradation of cellulose are the so called degradation of cellulose from the reducing end of its molecule and the alkaline hydrolysis of glycosidic bonds. The former process is observed almost exclusively at temperatures up to 150°C; the two processes occur simultaneously above this temperature.

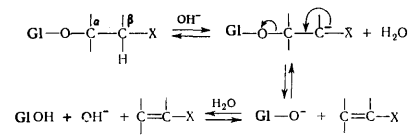
(*a*) Degradation of cellulose from the reducing end

The action of alkalis on cellulose at temperatures up to 150°C produces losses in weight without any considerable change in the degree of polymerisation [9,10]. Native cotton cellulose reacts slowly with a hot alkali solution, but the rate increases when the degree of polymerisation is lowered by hydrolysis, with a resulting increase in the number of aldehyde groups. On the basis of these observations Davidson suggested [11] that degradation consists in the successive detachment of units from the end of a molecular chain possessing reducing properties. The validity of this hypothesis has since been confirmed by numerous experimental data. It has been shown that hydrocelluloses are degraded more rapidly than cotton cellulose, though having the same chemical structure but a lower degree of polymerisation; the rate of degradation of hydrocelluloses increases as the degree of polymerisation falls, and hence as the content of reducing terminal groups decreases [10,12]. The stability of hydrocellulose towards hot dilute alkali is sharply improved when the aldehyde end-groups are eliminated by being oxidised to carboxy-groups with chlorous acid [13], bisulphite solutions at high temperatures [14], or cuprammonium solutions [15], reduced with sodium tetrahydroborate in weakly alkaline medium [10,16], dehydrated by heating [17], or even modified by glycoside formation [18].

Breakdown from the reducing end is indicated also by data suggesting that acids of approximately the same composition are formed by the action of alkalis on hydrocellulose and on 4-*O*-substituted monosaccharides and 1,4-disaccharides [19].

(*b*) Mechanism of degradation from the reducing end

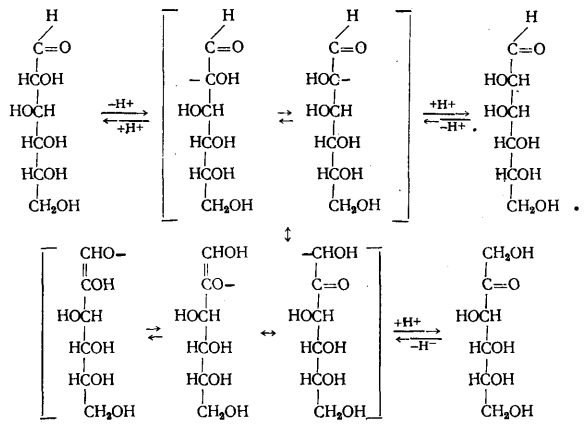
The most widely accepted explanation of the alkaline degradation of cellulose from the reducing end is based on Isbell's theory of β-elimination [20], which he proposed to explain the previously observed [21,22] instability towards alkalis of glycosides of alcohols containing electronegative groups in the β-position. The reaction is represented by



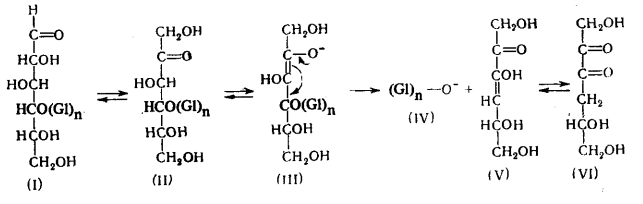
This theory is widely used at the present time to explain the sensitivity to alkalis of unsubstituted and substituted monosaccharides and also of di-, oligo-, and polysaccharides [19,23–35].

According to Isbell's theory an alkoxy-group should be present in the β-position relative to the aldehyde group. In the reducing terminal unit of cellulose the alkoxyl is in the γ-position to the aldehyde group. Detachment of the reducing terminal glucose unit will become possible after isomerisation into a fructose unit [9,23]. The possibility of the conversion of monosaccharides into their epimers and the corresponding ketoses by the action of alkalis had already been shown at the end of the nineteenth century by Lobry de Bruyn and van Ekenstein [36]. Not only monosaccharides but also the reducing units of disaccharides, oligosaccharides [37-40], and cellulose [23] are able to undergo similar transformations.

The most probable mechanism of this rearrangement [36] involves elimination of a proton and formation of a carbanion in equilibrium with enolate ions; the latter have a planar configuration and are converted with almost equal probability into three epimers [41]:

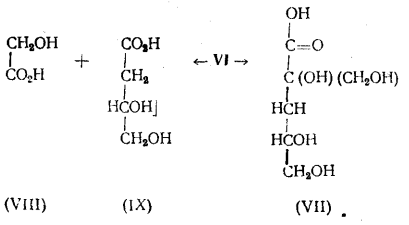


The degradation of cellulose by the action of alkalis is regarded [23] as involving conversion of a reducing terminal unit (I) of cellulose into a fructose unit (II), which is detached as the enolic form (V) of a dicarbonyl compound:



This liberates a reducing group in the adjacent glucose unit, which in turn undergoes the same changes. Thus a stepwise process of alkaline degradation takes place, beginning from that terminal unit of the cellulose molecule that possesses reducing properties.

The eliminated enol (V) undergoes further changes, the composition of the products depending on the nature of the alkali and the reaction conditions. Calcium hydroxide yields mainly D-glucoisosaccharinic acid (VII), whose formation results from rearrangement of 4-deoxy-D-*glycero*-2,3-hexodiulose (VI), which has been isolated from and identified in the products of the alkaline degradation of cellobiose [31] and maltose [32]:



Treatment with caustic soda favours conversion of (VI) into a mixture of $\beta\gamma$-dihydroxybutyric (IX), glycollic (VIII), formic, and lactic acids [19,32].

(*c*) "Stopping" reactions

The alkaline degradation of cellulose never goes to completion, and the final polysaccharide becomes stable towards alkali [10]. This stability is due to conversion of the usual reducing terminal glucose units into non-reducing units containing carboxy-groups [42,43]. Richtzenhain and Abrahamsson [44] considered that the reducing terminal units might rearrange into saccharinic acids, whereas Lindberg [45] assumed that the carboxyls were formed either by oxidation of the reducing groups by traces of oxygen or as a consequence of a Cannizzaro reaction between aldehyde groups of the terminal unit and those of soluble decomposition products.

The nature of the stabilising reaction was investigated by Machell and Richards [9,35], who subjected alkali-stabilised hydrocellulose to acid hydrolysis and isolated the acidic products. The main product was identified as D-metasaccharinic acid, whose formation during alkaline treatment might be a consequence of β-elimination of the 3-hydroxyl in the terminal glucose unit followed by rearrangement of the resulting enol. Because of the absence of a carbonyl group, hydrocellulose molecules containing metasaccharinic acid as terminal unit are stable towards alkali.

Alkaline-earth metal ions—Ca^{2+}, Sr^{2+}, Ba^{2+}—are evidently more effective than sodium ions in catalysing the conversion of reducing terminal units in cellulose into metasaccharinic acid redidues [12,33,46]. Stabilisation is usually slower than degradation from the reducing end. The activation energies for the degradation of hydrocellulose from the reducing end by the action of 5% sodium hydroxide solution (in the absence of oxygen) and for the formation of stable terminal metasaccharinic acid units are 24 and 32 kcal mole^{-1} respectively [47].

It is interesting that the 3-deoxy-D-*erythro*-hexulose postulated by Isbell's theory as an intermediate in the formation of metasaccharinic acids has been isolated and identified by Machell and Richards [34] on treating 3-*O*-benzyl-D-glucose with 0.04 *N* sodium hydroxide. On treating with calcium hydroxide solution the isolated reaction intermediate was converted almost quantitatively into D-glucometasaccharinic acid [34].

(*d*) Alkaline hydrolysis of glycosidic bonds

Solutions of alkalis at 170°C and above cause the direct hydrolysis of cellulose, which is indicated by a rapid drop in degree of polymerisation and considerable weight losses [48,49]. This reaction is due to the action of hydroxide

ions, not to oxidation by traces of oxygen or to a purely thermal effect [49]. Brooks and Thompson [50] used methyl β-glucoside to show that 10% sodium hydroxide solution produces a very low rate of rupture of glycosidic bonds (after 5 h only 0.3%, 0.9%, and 5.5% of glycosidic bonds broken at 140°, 150°, and 170°C respectively).

Investigation of the alkaline hydrolysis of glycosides by Lindberg and his coworkers [45, 51-54] on numerous model compounds showed the simultaneous occurrence of several reactions. Thus the action of 10% sodium hydroxide solution on 4-*O*-β-D-glucopyranosyl-D-sorbitol yields 1,6-anhydro-β-D-glucopyranose, D-sorbitol, 1,4-anhydro-D-sorbitol, and acidic products. Formation of the first two products necessitates rupture of the bond between the glycosidic oxygen and the $C_{(1)}$ atom of the glucose residue; formation of the third product requires rupture of the corresponding bond with the $C_{(4)}$ atom of the sorbitol residue. Direct attack by a hydroxide ion on these carbon atoms may give glucose and sorbitol respectively. Under the experimental conditions glucose rapidly forms acidic products.

The alkaline hydrolysis of cellulose forms new reactive groups for ensuring degradation from the reducing end, which occurs by the same mechanism as at lower temperatures. The soluble breakdown products obtained when cotton cellulose is treated with 0.5 *N* sodium hydroxide solution at 170°C include the same compounds as produced by treating hydrocellulose with a 0.5 *N* solution of the alkali at 100°C. [49]

2. Alkaline Degradation of Oxidised Celluloses

Since oxidation and alkaline degradation occur simultaneously, it is useful first to examine the alkaline degradation of already oxidised cellulose. Alkalis break down the structure of oxidised celluloses. Davidson investigated the oxidation of cellulose with potassium dichromate in an acid medium, and found that the viscosity of a solution of oxidised cellulose nitrate is far higher than that of oxidised cellulose in cuprammonium solution. This difference disappears after treatment of the oxidised cellulose with alkali [55]. Furthermore, oxidised celluloses lose weight when heated with weak solutions of alkalis [56]. Staudinger and Sohn [57] attributed the lowering of the degree of polymerisation of cellulose to the presence of ester bonds in its chain, which are cleaved by the action of alkalis. They also discussed the ways in which ester bonds are formed on oxidation.

Somewhat later, investigators came to link the degradation of oxidised celluloses by the action of alkalis with the formation of carbonyl groups, which facilitate the rupture of glycosidic bonds [58, 59]. Oxycelluloses obtained by periodate oxidation, and hence containing aldehyde groups at positions 2 and 3 of the repeating unit of cellulose [60], are easily degraded by alkalis [13, 56, 61-63], the sensitivity to which increases with increase in the content of aldehyde groups [61, 63]. According to Kaverzneva and Ivanov the fall in the viscosity of cellulose when oxidised with air in cuprammonium solution is due to rupture of glycosidic bonds caused by the presence of aldehyde groups formed by the oxidation of primary alcoholic groups [64].

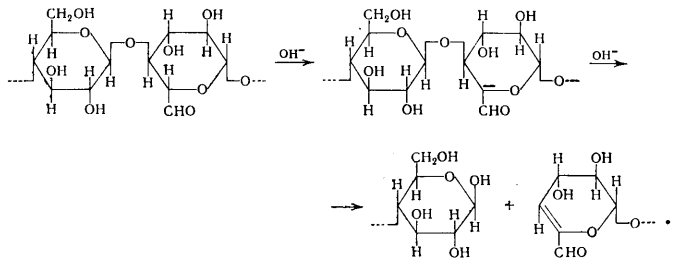
The influence of ketonic groups on the stability of cellulose oxidised with dichromate was referred to by Meller [13]. Kaverzneva and Kist' [65] showed that the presence of a considerable quantity of ketonic groups in cellulose oxidised with nitrogen dioxide is the main reason for its degradation in alkaline media.

The dominant effect of carbonyl groups on the degradation of oxidised cellulose in an alkaline medium is evident also from the conversion of alkali-unstable oxidised celluloses into stable materials by reduction with sodium tetrahydroborate in a weakly alkaline medium, i.e. under conditions such that aldehyde groups are converted into alcoholic groups [61-63, 66]. The stability of oxidised celluloses is considerably enhanced also when carbonyl groups are oxidised to carboxy-groups [13, 62].

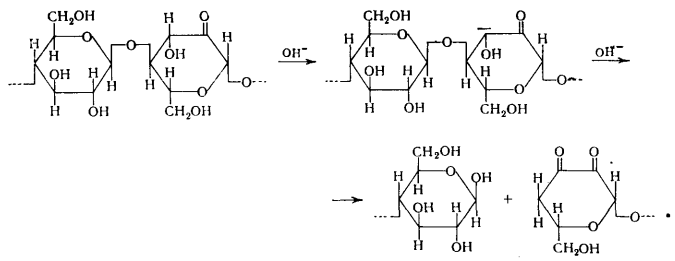
(*a*) Mechanisms of the degradation of oxidised celluloses

Several reaction mechanisms have been suggested [58, 64, 67, 68] to explain the alkaline degradation of oxidised celluloses, but investigations during recent years of the degradation of these materials, as well as of monosaccharides, disaccharides, and their derivatives, have shown that, when a carbonyl group is present in the β-position relative to a glycosidic bond, degradation takes place mainly by Isbell's mechanism [69].

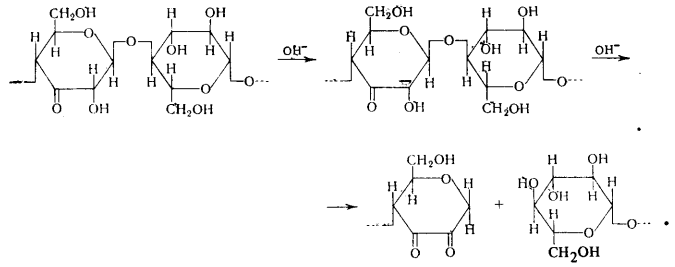
This hypothesis was first put forward by Haskins and Hogsed [59], who gave the following scheme for the alkaline degradation of cellulose containing units with a 6-aldehyde group



When the alcoholic group at $C_{(2)}$ of the repeating unit of cellulose is oxidised, the mechanism of cleavage of the glycosidic bond under the influence of alkali will be

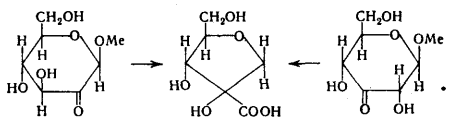


The action of alkali on cellulose containing units with a 3-keto-group should be represented by



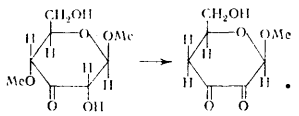
A later investigation of the action of alkali on model compounds having a keto-group at the $C_{(2)}$ and $C_{(3)}$ atoms—methyl β-D-*arabino*-hexulopyranoside (X) and methyl

β-D-*ribo*-3-hexulopyranoside (XI)—showed [70] that they rapidly split off the methoxy-group under the influence of weak solutions of sodium or calcium hydroxide at room temperature. The same final product (XII) is obtained in the two cases, whence it follows that the intermediate product is the same in the two reactions:



(X) (XII) (XI)

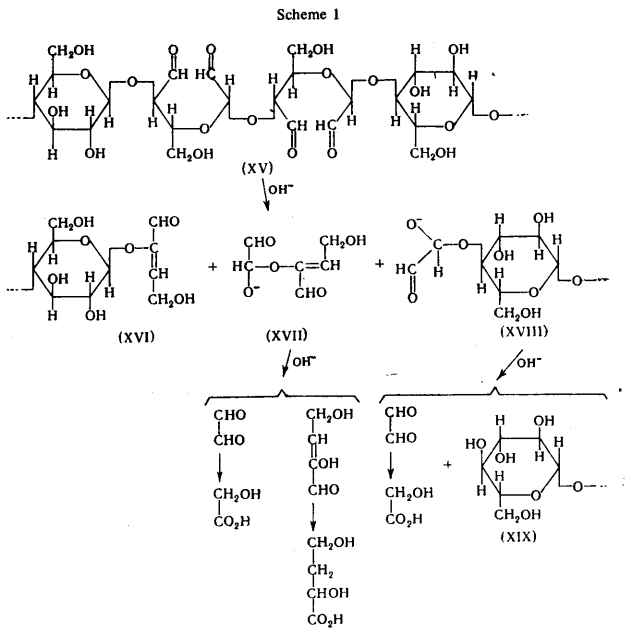
In order to determine whether, in the alkaline treatment of cellulose containing glucose units with a keto-group at $C_{(2)}$or $C_{(3)}$, elimination occurs at the glucosidic carbon atom or at the $C_{(4)}$ atom, the alkaline degradation of methyl 4-*O*-methyl-β-D-*ribo*-3-hexulopyranoside (XIII) was examined [71]. This compound is degraded almost five times as rapidly as (XI). The chief intermediate product is isolated in the degradation of (XIII) was the 4-deoxy-compound (XIV):



(XIII) (XIV)

From this the author concluded that the alkaline degradation of oxidised cellulose of this type involves the cleavage mainly of bonds between the $C_{(4)}$ atoms of the glucose units and the oxygen of the glycosidic bonds.

Scheme 1



Model compounds—methyl 4-*O*-methyl-β-D-*arabino*-hexulopyranoside, methyl 4-*O*-methyl-β-D-*ribo*-3-hexulopyranoside, and methyl 6-formyl-4-*O*-methyl-β-D-glucopyranoside—were used to study the effect of different positions of the carbonyl group in the oxidised glucose unit. The glycosidic bond was found to be most labile in compounds containing a carbonyl group in position 2 or 3. It was more stable in compounds containing a 6-aldehyde group [71].

O'Meara and Richards [69] examined the initial and final products of the alkaline degradation of periodate-oxidised cellulose, and concluded that degradation occurs mainly by Isbell's β-alkoxy-carbonyl mechanism. When periodate oxycellulose is treated with calcium hydroxide solution the chief products are glycollic and αβ-dihydroxybutyric acids, the relative proportion of the former acid diminishing with increasing degree of oxidation of the cellulose. These workers give Scheme 1 for the degradation of periodate-oxidised cellulose.

Three cleavage products (XVI)–(XVIII) are formed initially. The first of these is fairly resistant to the further action of alkali. Products (XVII) and (XVIII) are glyoxal hemiacetals, and are rapidly cleaved by lime-water at room temperature: (XVII) gives equivalent quantities of glycollic and αγ-dihydroxybutyric acids; and (XVIII) yields glycollic acid and a normal, non-reducing terminal glucose unit (XIX). The possibility of such breakdown is supported by a study of the properties of glyoxal hemiacetals [69] and of the alkaline decomposition of model compounds [72]. The ratio of the quantities of glycollic and αγ-dihydroxybutyric acids for cellulose preparations of different degrees of oxidation also supports reaction in this direction, since only the product (XVII), which is formed at a high degree of oxidation of the cellulose, is a source of αγ-dihydroxybutyric acid.

III. OXIDATION OF CELLULOSE BY MOLECULAR OXYGEN IN ALKALINE MEDIA

In the preceding Sections of the Review we have isolated and examined aspects of the alkaline degradation of cellulose and oxycelluloses. We now give an account of published information on the simultaneous oxidative and alkaline degradation of cellulose. The oxidation of cellulose by air in alkaline media can take place both under heterogeneous and under homogeneous conditions. Processes involving the heterogeneous oxidation of cellulose are especially widespread, taking place both in the isolation and processing of cellulose and during the functioning of goods made from it. The Review will be confined to aspects of the heterogeneous oxidation of cellulose.

Most of the many publications on the oxidation of cellulose by molecular oxygen in an alkaline medium are concerned with the investigation of oxidation under the conditions of ripening in the manufacture of viscose rayon. We shall first give the experimental results obtained by various investigators on the oxidation of cellulose by molecular oxygen in alkaline media, and then consider views on the chemical changes undergone by the cellulose macromolecule and the suggested reaction schemes.

1. Process Characteristics of the Oxidation of Cellulose

The autoxidation of cellulose in alkaline media has been followed experimentally by examining the rate of absorption of oxygen, the variation in degree of polymerisation and in functional groups, and the chemical composition of the resulting cellulose and decomposition products of low molecular weight. The first fact to emerge from an examination of these results is that the rate and several features of the oxidation depend in considerable measure on whether the cellulose has been squeezed free from

excess of alkali or whether oxygen is passed through caustic soda solution containing cellulose in suspension. For the sake of brevity we shall henceforward term the former process the "oxidation of alkaline cellulose", and the latter the "oxidation of a cellulose suspension". When discussing the autoxidation of alkaline cellulose the alkali concentration will not be indicated if 18–20% solutions of caustic soda were used for impregnation. The oxidation of a suspension of cellulose is slower than that of alkaline cellulose.

Mention should be made of the difficulties of comparing results obtained by different workers, resulting from the use of different samples of cellulose, obtained not only from different types of raw material but also by different methods of isolation and purification, and resulting also from the use of different methods for determining functional groups and different degrees of polymerisation of the cellulose. Different methods often give different results.

Here we shall not consider the defects of methods for determining functional groups in cellulose, but merely cite the literature on this problem. Critical surveys of such methods will be found in monographs[3,73,74]. Analytical results for carbonyl groups obtained by various methods have been compared by the Sihtola[75], Strole[76], and Gunne and Samuelson[77]. Different methods for determining the copper numbers of cellulose were compared by Bethge and Nevell[78], and copper numbers have been compared with the content of carbonyl groups determined by the hydroborate method[79]. Various methods have been given[80,81] for determining carboxy-groups.

(*a*) Absorption of oxygen

The chief parameter indicating the rate of autoxidation of cellulose is the rate of absorption of oxygen. It must be borne in mind, however, that the oxygen absorbed is consumed not only in the primary oxidation of cellulose macromolecules but also in the oxidation of secondary products of low and high molecular weight, formed as a result of oxidative–alkaline degradation. The rate curves for the absorption of oxygen during the oxidation of alkaline cellulose comprise three portions: the rate varies during the first period, after which it remains constant, and during the third period it falls[82–84].

For any given type of cellulose the initial rate of absorption of oxygen during oxidation of the alkaline material is proportional to the copper number of the regenerated cellulose. The same dependence is shown by cotton cellulose bleached with hypochlorite, hydrocellulose obtained from cotton cellulose, and various wood celluloses. The initial rate of absorption of oxygen by periodate-oxidised cellulose is about half the rate for cotton cellulose and other celluloses having the same copper numbers as the periodate-oxidised sample. A diminished initial rate of absorption of oxygen was observed also for cellulose that had first been subjected to oxidation by molecular oxygen in an alkaline medium. If oxidation was interrupted during the constant-rate period, and the regenerated cellulose was again subjected to oxidation, the rate of absorption of oxygen was very low, far below the steady rate, although the regenerated cellulose had a high copper number. The explanation offered was that probably not all, only a proportion, of the reducing groups of cellulose are capable of initiating its oxidation[84].

In some cases oxidation progresses autocatalytically during the first period: i.e. the rate of absorption of oxygen increases with the duration of oxidation. Purified cotton cellulose, of low reducing power, is oxidised autocatalytically. In other cases the rate of absorption of oxygen gradually decreases, as in the oxidation of wood celluloses of higher reducing power[84]. Sometimes the rate of absorption of oxygen remains constant from the start of oxidation, as with alkaline purified beechwood cellulose[82].

During the second period of oxidation the rate of absorption of oxygen is constant and about the same for different alkaline celluloses, in spite of differences in reducing power[84]. The rate remains constant until the total absorption is ~0.6 oxygen atom per anhydroglucose unit of the cellulose[84].

With increase in the alkali concentration the rate of absorption of oxygen by alkaline cellulose increases, passes through a maximum, and decreases with further increase in concentration. Weltzien and Tobel[85] observed the maximum rates at alkali concentrations of 6.5 *N* and 8.5 *N* for cotton cellulose and for cellulose hydrate regenerated from cuprammonium solution respectively, and Davidson[83] found the optimum for cotton cellulose to be 10 *N* caustic soda. With wood cellulose the maximum rate of absorption of oxygen is found at a concentration of the impregnating alkali of 10–12.5 *N*.[84]

Not only the rate of absorption of oxygen but also the character of the rate curves changes with the alkali concentration for the same cellulose preparation. At alkali concentrations below 8 *N* the initial rate exceeds the steady value in the oxidation both of alkaline cellulose and of a suspension of cellulose; above 8 *N*, however, the initial rate is lower than the steady rate[84,86]. In the oxidation of a suspension of cellulose, in contrast to that of alkaline cellulose, the rate of absorption of oxygen increases continuously with increase in the alkali concentration[86].

A rise in temperature produces an increase in the rate of absorption of oxygen[83–85]. According to Davidson[83] the rate increases approximately ninefold when the temperature of the oxidation of alkaline cotton cellulose is raised from 20° to 40°C. Entwistle et al.[84] calculated the activation energy as ~21 kcal mole^{-1} for sulphite wood cellulose during the period of a steady rate of absorption of oxygen by the alkaline material at temperatures from 5° to 80°C. This value corresponds roughly to a threefold increase in reaction velocity for a 10-deg rise in temperature.

Increase in the oxygen pressure from 25 to 700 mmHg produces an increase in the rate of absorption. At higher alkali concentrations the rate is more strongly dependent on pressure[84,86].

Salts of various metals present in low concentrations in cellulose have an appreciable catalytic effect on its rate of oxidation. Those of iron[87], copper[83], nickel[83], cobalt[86], and manganese at a manganese concentration of 0.002% (on the cellulose)[87,88] are positive catalysts. The greatest effect is exerted by salts of cobalt, followed by manganese, iron, nickel[88], and copper[89]. Gold and silver salts are inhibitors, as also manganese salts at manganese concentrations exceeding 0.05%.[88] Neither catalytic nor inhibiting metal salts have any appreciable effect on the initial rate of absorption of oxygen, but affect it during subsequent stages of the reaction[88].

The addition of substances that form free radicals increases the initial rate of absorption of oxygen[88].

Addition of 0.1% of a typical antioxidation to the impregnating alkali lowers appreciably the steady rate of absorption of oxygen. 1,4-Naphthaquinone and magnesium diphenylamine-*p*-sulphonate were most effective[88].

These antioxidants did not influence the initial rate of absorption.

The initial rate is increased by adding to the impregnating alkali substances capable of autoxidation, such as glucose, formaldehyde, sodium dithionite, etc.[88]

If oxidation is interrupted by removing oxygen from the reaction space, and is then renewed, the original rate of absorption of oxygen is re-established[82,83].

(*b*) Variation of degree of polymerisation of cellulose during oxidation in alkaline media

The degree of polymerisation of cellulose usually drops sharply at the beginning of oxidation, but the rate of depolymerisation then diminishes[84,90-93]. A high rate of depolymerisation during the initial period is observed[94-96] in celluloses having a comparatively high content of carbonyl groups and hence high copper numbers (0.58 to 1.04 according to Brady). In celluloses having low contents of carbonyl groups (Brady copper numbers 0.10–0.18) the rate of depolymerisation remained constant for 24 h. Reduction with sodium tetrahydroborate to diminish the content of carbonyl groups in wood celluloses only slightly decreases the rate of depolymerisation during the first period of oxidation. During the following period the rates for reduced and unreduced cellulose converge, with the rate for celluloses in which the carbonyl groups have been reduced remaining constant[94].

Good agreement was shown[84] between the initial rate of absorption of oxygen by alkaline wood celluloses and the rate of decrease in viscosity, as well as the same ratio of change in viscosity to quantity of oxygen absorbed by alkaline cotton cellulose of varying reducing power. Schulz and Mertes[82] compared their kinetic data on oxygen absorption with the variation in degree of polymerisation during the oxidation of alkaline cellulose at 20°C. They observed a rapid fall in degree of polymerisation at the start of the oxidation of alkaline cotton cellulose, after which depolymerisation slowed down, and a constant rate was established after about 15 h. The rate of absorption of oxygen became constant 100 h after the start of oxidation. In the oxidation of beechwood cellulose under the same conditions the rate of depolymerisation was constant from the very beginning.

The rate of depolymerisation of cellulose during oxidation depends on the caustic soda concentration. At low alkali concentrations cellulose is depolymerised very slowly. For example, the degree of polymerisation hardly changes during the oxidation of a cellulose suspension in 1% and 2% caustic soda solution at 40°C,[97] and varies very slightly during oxidation at 85–86°C.[98] With alkali concentrations up to 80 g litre^{-1} no change in degree of polymerisation occurs for 2 h during the oxidation both of alkaline cellulose and of a cellulose suspension at 50°C. With increase in the caustic soda concentration the rate of depolymerisation of cellulose passes through a maximum according to some investigators[86,99,100] but exhibits a continuous increase according to others[83,89]. The reasons for the discrepancies are obscure.

The rate of depolymerisation of cellulose increases with rise in temperature[99,101,102]. It has been suggested that the mechanism of degradation in the oxidation of alkaline cellulose is probably the same at different temperatures (25° and 50°C), a difference being observed only in the rate of degradation[103].

Catalysis of the oxidation of alkaline cellulose by transition-metal compounds or free radicals is accompanied by increase in the degree of depolymerisation for a given absorption of oxygen[83,88]. In the presence of silver and organic antioxidants the degree of depolymerisation at a given oxygen absorption decreases[83,88]. The introduction of hydrogen peroxide considerably accelerates the rate of depolymerisation during oxidation by molecular oxygen both of alkaline cellulose[104-106] and of a cellulose suspension[107]; the rate of depolymerisation increases with increase in the hydrogen peroxide concentration. Additions to cellulose of sodium sulphide[104], sodium hypochlorite[104,108], and ammonium persulphate (in amounts of 1–8%)[104] accelerate the depolymerisation of alkaline cellulose. The presence in the impregnating alkali of 1% of substances capable of autoxidation, such as glucose and sodium dithionite, has little effect on the rate of depolymerisation of cellulose.

(*c*) Change in functional groups during oxidation of cellulose

An important feature of the oxidation of cellulose is the formation of carbonyl and carboxyl groups in the macromolecules.

According to Davidson[83] and to Entwistle et al.[84] the reducing power of cellulose, as measured by the copper number, increases continuously during the oxidation of alkaline cellulose by molecular oxygen. According to other workers[81,94,109] the reducing power increases only during the first few hours of oxidation, after which it remains almost unchanged. For a given oxygen absorption the content of aldehyde groups is larger with higher alkali concentrations and in the presence of oxidation catalysts[83,88]. Only a slight change in copper number was observed[97] during the oxidation of a suspension of cellulose.

Both aldehydic and ketonic groups are formed in the oxidation of alkaline cellulose[77]. It is not surprising that the reducing power of cellulose observed during oxidation is slight, since in alkaline media the carbonyl groups undergo further oxidation or the other reactions described earlier. The content of carboxy-groups gradually increases with increasing duration of oxidation[81,84,88,109,110]. At a given oxygen absorption the carboxyl content is greater in the presence of cobalt[88].

The oxidation of alkaline cellulose by molecular oxygen involves the formation of peroxides[84,99,111], the quantity of which diminishes in the presence of traces of salts of metals that catalyse oxidation (cobalt, manganese) and also metals that inhibit oxidation (silver). No peroxide at all could be detected in the presence of 0.0006% of cobalt or 0.0032% of silver[84,88].

(*d*) Chemical composition of products of the oxidative–alkaline degradation of cellulose

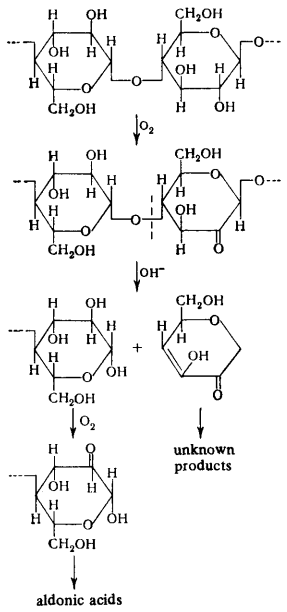
Examination of the changes in functional groups and degree of polymerisation during oxidation by molecular oxygen still does not provide an accurate idea of the chemical changes undergone by the cellulose molecule. It is true that the fact that a small quantity of absorbed oxygen produces a considerable change in degree of polymerisation indicates that oxidation occurs throughout the length of the cellulose molecule, not only at its ends. It was suggested that oxygen would attack preferentially carbon atoms carrying the most ionised hydroxy-groups, i.e. the second carbon atom in the repeating unit[84].

However, a more exact picture of the reaction mechanism can be obtained only from a study of the structure of the oxidation products—both those of low molecular weight, which pass into solution, and those of high molecular weight, remaining in the solid phase.

The chemical composition of cellulose remaining after oxidation with molecular oxygen in an alkaline medium depends on the conditions. The only acid found after the oxidation of cellulose hydrate suspended in 1% caustic soda solution in air at 100°C was erythronic acid [112]. Arabonic acid was found, with smaller quantities of erythronic and mannonic acids, in the oxidised cellulose formed from alkaline cellulose at 33°C; small quantities of gluconic and ribonic acids were also detected [113].

According to a hypothetical scheme to explain the formation on erythronic acid [112] the main reaction involves oxidation of the secondary alcoholic groups at $C_{(2)}$ and $C_{(3)}$ to keto-groups with subsequent oxidation to the dicarboxylic acid, which in turn is oxidised to a carbonic ester. Hydrolysis of the ester in an alkaline medium results in cleavage of the macromolecules to give an erythronic acid residue at the end of one newly formed cellulose molecule, and a non-reducing anhydroglucose unit at the end of the other molecule [112].

Scheme 2



Another series of reactions (Scheme 2) has been suggested for the oxidative degradation of alkaline cellulose by workers [113] who found that the oxidised cellulose contained as terminal units arabonic, erythronic, mallonic, gluconic, and ribonic acids in roughly the same proportions as are formed in the oxidation of glucose and cellobiose under similar conditions [114]. On the basis of this observation it was suggested [113] that the terminal aldonic-acid units were formed by the oxidation of reducing terminal glucose units in the cellulose.

2. Mechanism of the Oxidation of Cellulose by Molecular Oxygen in Alkaline Media

(*a*) Radical-chain mechanism of the oxidation of cellulose

During the past two decades investigators have begun to work on elucidating the mechanism of the oxidation of cellulose by molecular oxygen in alkaline media. The first papers on this problem were published in 1949 by Entwistle, Cole, and Wooding [84,88], who suggested a radical-chain mechanism analogous to that of the autoxidation of alkenes. They based it on kinetic data on the absorption of oxygen by alkaline cellulose during oxidation, observations on the catalytic action of transition-metal ions, inhibition by silver and organic antioxidants, the increase in the initial rate of oxidation on the addition of substances that dissociate to form free radicals, and the relation between the initial rate of oxidation and the content of reducing groups. This mechanism includes the stages indicated in the subheadings below.

Chain initiation. The autoxidation of alkaline cellulose begins by the detachment of an active hydrogen atom by molecular oxygen. In cellulose the hydrogen of an aldehyde group (perhaps enolised) is active:

$$R_{cell}-C(=O)H + O_2 \rightarrow HOO^{\cdot} + R_{cell}-C^{\cdot}=O \quad (1)$$

The resulting cellulose radical then reacts as follows:

$$R_{cell}-C^{\cdot}=O + O_2 \rightarrow R_{cell}-CO(OO^{\cdot}) \quad (2)$$

$$R_{cell}-CO(OO^{\cdot}) + R_{cell}-H \rightarrow R_{cell}-CO(OOH) + R_{cell}^{\cdot} \quad (3)$$

Entwistle and his coworkers put forward the hypothesis that the allylic hydrogen in an enolised reducing thermal unit of cellulose should be especially labile, and removable by molecular oxygen:

$$R_{cell}-OCH(CHOH-CH_2OH)-C(OH)=CHO^- + O_2 \rightarrow R_{cell}-OCH(CHOH-CH_2OH)-\dot{C}(OH)-C(OH)=CHO^- + HOO^{\cdot}$$

These workers assume [84] that oxidation is facilitated by ionisation of the hydroxy-groups of cellulose. The presence of an ionised hydroxyl on a carbon atom attached to hydrogen may strongly polarise and weaken the carbon-hydrogen bond. Oxidising attack in an unchanged repeating unit of cellulose probably takes place at the carbon atom having the most ionised hydroxyl, and hence primarily at the second carbon atom of the anhydroglucose unit.

Chain propagation. Subsequent oxidation of the cellulose takes place by alternation of the reactions

$$R_{cell}^{\cdot} + O_2 \rightarrow R_{cell}-OO^{\cdot} \quad (4)$$

$$R_{cell}-OO^{\cdot} + R_{cell}-H \rightarrow R_{cell}-OOH + R_{cell}^{\cdot} \quad (5)$$

and the hydroperoxy-radical detaches a hydrogen atom from a carbon atom of a repeating unit. In an alkaline medium the resulting hydroperoxides are usually hydrolysed to form hydrogen peroxide:

$$R_{cell}-OOH + H_2O \rightarrow R_{cell}-OH + H_2O_2 \quad (6)$$

After the hydrolysis of hydroperoxides formed on the second, third, or sixth carbon atom of the repeating unit, hydrated forms of the ketone or aldehyde are produced, which immediately lose water to give a keto- or aldehydo-cellulose. If the hydroperoxide has been formed on the

fourth or fifth carbon atom, hydrolysis yields a hemiacetal, which is rapidly hydrolysed with cleavage of the cellulose molecule. Hydrolysis of a hydroperoxide on the first carbon atom produces an orthoester, which in an alkaline medium is also rapidly hydrolysed with rupture of the chain.

The hydroperoxide formed may also undergo homolytic decomposition to give a free radical on the cellulose and a free hydroxy-radical, so that chain branching occurs:

$$R_{cell}\cdot OOH \rightarrow R_{cell}-O^{\cdot} + HO^{\cdot}. \qquad (7)$$

Homolytic decomposition of hydroperoxides is accelerated in the presence of catalytically active metals:

$$R_{cell}-OOH + M^{2+} \rightarrow R_{cell}-O^{\cdot} + HO^{-} + M^{3+}. \qquad (8)$$

Thus the catalytic effect of metals emphasises the radical-chain character of the reaction, although oxidation may take place in their absence. When transition-metal ions are not present, a cellulose hydroperoxide will break down mainly with the liberation of hydrogen peroxide by reaction (6).

Chain termination. Termination may be caused by the association of radicals or by the reaction of radicals with impurities. Since alcohols and carbohydrates can be active inhibitors of chain reactions, it was assumed [84] that the reaction chains might be relatively short.

A weighty argument in favour of the formation of free radicals in the macromolecule in the oxidation of alkaline cellulose is Schurz's observation of the formation of a graft copolymer by the action of styrene on the spontaneously oxidising alkaline cellulose system: a homopolymer is not formed. However, the life of the radicals is very brief, especially at high temperatures. In this worker's opinion the long-lived groups initiating the graft copolymerisation after oxidation has ceased are peroxy-groups in the cellulose, which on heating give free radicals [115]. However, Mottor's attempts to detect free radicals by electron spin resonance were unsuccessful [116]. Determination of the quantity of hydroxyl radicals by a chemical method based on the convertion of benzene into phenol showed their almost complete absence.

(*b*) Ionic mechanism for the oxidation of cellulose

In view of his finding that hydroxyl radicals are absent, Mottor assumes [116] that the autoxidation of alkaline cellulose takes place by an ionic mechanism. Oxygen is regarded as reacting initially with reducing functional groups in the cellulose, probably aldehyde groups, which in an alkaline medium behave as Lewis acids and form the anions (XX) and (XXI):

$$R_{cell}-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{C}} \underset{\rightleftharpoons}{\overset{HO^-}{\rightarrow}} R_{cell}-\underset{OH}{\overset{O^-}{C}}-H \underset{\rightleftharpoons}{\overset{HO^-}{\rightarrow}} R_{cell}-\underset{O^-}{\overset{O^-}{C}}-H + H_2O. \qquad (9)$$

(XX) (XXI)

These anions are able to donate a hydride ion to an oxygen molecule to form a hydrogen peroxide ion:

$$R_{cell}-\underset{O^-}{\overset{O^-}{C}}-H + O_2 \rightarrow R_{cell}-\underset{O^-}{\overset{O}{C}} + HOO^-, \qquad (10)$$

which oxidises the cellulose.

The ability of hydrogen peroxide to oxidise cellulose is well known [105,117,118]. Kleinert showed that the changes occurring in the oxidation of alkaline cellulose are analogous to those accompanying the oxidation of cellulose by hydrogen peroxide in 18% caustic soda [105].

(*c*) Ion–radical chain mechanism for the oxidation of cellulose

MacDonald [107] combined the two views on the autoxidation of alkaline cellulose and suggested that the initial stages take place by an ionic mechanism, and later stages by a radical mechanism. On the basis of Mottor's results showing the absence of hydroxyl or perhydroxyl radicals during the autoxidation of alkaline cellulose, those of other workers on the effect of transition-metal ions on the formation of hydrogen peroxide and the fall in the viscosity of cellulose, and also his own results on the inhibition of autoxidation by sulphur and on the quantity of hydrogen peroxide formed during the autoxidation of cellulose suspended in caustic soda solution [107], MacDonald considers that at the start of the process, when the reducing groups of the cellulose are undergoing oxidation, hydrogen peroxide can be formed only by Mottor's ionic mechanism (reactions 9 and 10). In the presence of metal catalysts the resulting hydrogen peroxide would form cellulose free radicals but not hydroxyl or perhydroxyl radicals. MacDonald considers that the cellulose radicals are formed by detachment of a hydrogen atom from cellulose by means of complexes of hydrogen peroxide ions with tervalent iron ion. Such complexes had been described by Kremer in a study of the decomposition of hydrogen peroxide by iron(III) salts [119]. The cellulose radicals then react by the chain mechanism suggested by Entwistle et al. (reactions 4–6). The oxidation products $R_{cell}OH$ undergo the further reactions described earlier.

A rather different mechanism was suggested by Michie and Neale [86] for the oxidation of cellulose in an alkaline medium. On the basis of their kinetic data on the absorption of oxygen by cellulose suspended in caustic soda solution, and also data obtained by other investigators on the autoxidation of alkaline cellulose, glucose, and α-ketols, they considered direct initiation of autoxidation by radicals formed by interaction between oxygen and reducing groups in the cellulose to be impossible. They assumed that initiation is effected by monomeric radicals formed by decomposition of hydroperoxides, the latter produced by the reducing groups at the start of the process. Transition-metal ions play an important part in the decomposition of the hydroperoxides. Oxidation then proceeds as in most cases of autoxidation. Formation of a cellulose radical is followed by absorption of oxygen with formation of the corresponding peroxy-radical. The latter radical would be extremely unstable, because hydroperoxides are hydrolysed rapidly in alkaline solution, and also because of the instability of compounds containing a peroxy- and a hydroxy-group attached to the same carbon atom. This radical may therefore be expected to break down rapidly to give an $HO_2^{\cdot}$ radical and a carbonyl group. Under alkaline conditions the $HO_2^{\cdot}$ radical will be almost completely dissociated into the radical ion $O_2^{\cdot -}$. The hydroperoxy-radical $HO_2^{\cdot}$ is known to be far less reactive than the hydroxyl radical $HO^{\cdot}$, [120] so that the ionised form of the former radical will probably be a still weaker oxidising agent. But these workers consider that the radical ion $O_2^{\cdot -}$ is nevertheless able to oxidise a cellulose molecule ionised in strongly alkaline medium.

Michie and Neale give the following scheme for the oxidation of cellulose:

(i) chain initiation

$$HO_2^- \rightarrow O_2^{\cdot -} \quad , \tag{11}$$

(ii) chain propagation

$$O_2^{\cdot -} + R_{cell}\text{—}\overset{|}{C}HO^- \rightarrow R_{cell}\text{—}\overset{|}{C}\cdot\text{—}O^- + HO_2^- \tag{12}$$

$$R_{cell}\text{—}\overset{|}{C}\cdot\text{—}O^- + O_2 \rightarrow R_{cell}\text{—}\overset{|}{C}\text{=}O + O_2^{\cdot -} \quad , \tag{13}$$

(iii) chain termination

$$R_{cell}\text{—}\overset{|}{C}\cdot\text{—}O^- + O_2^{\cdot -}(H^+) \rightarrow R_{cell}\text{—}\overset{|}{C}\text{=}O + HO_2^- \quad . \tag{14}$$

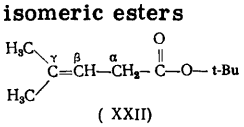
$$2\,O_2^{\cdot -} + H^+ \rightarrow HO_2^- + O_2 \tag{15}$$

Ionisation of the hydroxy-groups of cellulose and of a cellulose radical are represented by the equations

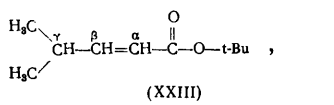
$$R_{cell}\text{—}\overset{|}{C}HOH + HO^- \rightarrow R_{cell}\text{—}\overset{|}{C}HO^- + H_2O \tag{16}$$

$$R_{cell}\text{—}\overset{|}{C}\cdot OH + HO^- \rightarrow R_{cell}\text{—}C\cdot\text{—}O^- + H_2O \quad . \tag{17}$$

Thus no generally accepted view has yet emerged on the mechanism of the oxidation of cellulose by molecular oxygen in alkaline media, as on the mechanism of the oxidation under analogous conditions of many compounds of low molecular weight. It may be supposed that, besides the above possible mechanisms of oxidation, some part in these processes will be played by the reactions of carbanions formed under the influence of the alkali. A basis for such a hypothesis is provided by data on the oxidation of esters and ketones in alkaline media with the formation of α-hydroxyperoxides [121,122]. This possibility is demonstrated still more clearly by results for the oxidation of the isomeric esters



(XXII)



(XXIII)

which in an alkaline medium give a considerable quantity of α-oxidised products, but only γ-hydroperoxides by true free-radical oxidation in benzene solution [123].

One possible oxidation mechanism involving carbanions is represented by the scheme [124-127]

$$\rangle C^- + O_2 \rightarrow \rangle C\cdot + O_2^{\cdot -} \tag{18}$$

$$\rangle C\cdot + O_2 \rightarrow \rangle COO\cdot \tag{19}$$

$$\rangle COO\cdot + \rangle C^- \rightarrow \rangle COO^- + \rangle C\cdot \quad . \tag{20}$$

In the classical free-radical mechanism of oxidation, initiation is effected by the detachment of a hydrogen atom from the oxidisable compound (e.g. Eqn. 1), but in the present case it occurs by electron transfer (Eqn. 18). If such a mechanism is accepted, the great ease of oxidation in the presence of alkalis compared with oxidation in neutral medium can be explained. Another mechanism is also possible for the oxidation of carbanions:

$$\rangle C^- + O_2 \rightarrow \rangle CO_2^- \quad . \tag{21}$$

However, there are grounds for thinking that this process is improbable [128].

Whatever the mechanism of oxidation, its result is always the formation of hydroperoxides (or hydroperoxy-radicals) as reaction intermediates. In alkaline media the hydroperoxides are hydrolysed with the formation of hydrogen peroxide, which is able to oxidise cellulose. Further support for this is given by Müller's results [99] showing that the degree of polymerisation of cellulose remains completely unchanged when alkaline cellulose is oxidised by molecular oxygen in the absence of water, whereas with an insufficient quantity of water it changes more slowly than during the oxidation of cellulose in the presence of a sufficient quantity. The absence of water probably slows down not only the rate of formation of hydroperoxides, owing to the diminished degree of ionisation of the cellulose hydroxyls, but also terminates the formation of hydrogen peroxide, because of the impossibility of the hydrolysis of hydroperoxides under anhydrous conditions.

Unfortunately, the mechanism of oxidation by hydrogen peroxide in an alkaline medium has not yet been accurately established. Most investigators adhere to a radical reaction mechanism: they consider that the active oxidising agent is the hydroxyl radical, formed by the decomposition of hydrogen peroxide in the alkaline medium. Kazarnovskii and Neiding [129] assume that the decomposition of hydrogen peroxide in alkaline solutions is caused by reaction between products of its electolytic dissociation and the undissociated molecules:

$$\left.\begin{aligned} H_2O_2 &= H^+ + HO_2^- \\ HO_2^- &= H^+ + O_2^{2-} \end{aligned}\right\} \text{electrolytic dissociation}$$

$$O_2^{2-} + H_2O_2 = O_2^{\cdot -} + OH^- + OH\cdot \quad \text{(chain initiation)}$$

$$\left.\begin{aligned} H_2O_2 + OH\cdot &= H_2O + HO_2\cdot \\ HO_2\cdot &= H^+ + O_2^{\cdot -} \\ H_2O_2 + O_2^{\cdot -} &= OH^- + O_2 + OH\cdot \end{aligned}\right\} \text{reaction chain} \quad .$$

Several investigators, however, hold a different view on the mechanism of the oxidising action of hydrogen peroxide, regarding the active agent as the anion HO_2^-. [130-132]

It must be supposed that further investigations on the mechanism of the oxidative-alkaline breakdown of cellulose under the influence of molecular oxygen in various media will establish the actual mechanism of these processes.

IV. EFFECT OF SUPERMOLECULAR STRUCTURE OF CELLULOSE ON ITS ALKALINE AND OXIDATIVE-ALKALINE DEGRADATION

The reactivity of cellulose, as of other biopolymers, is greatly dependent on its supermolecular structure. The ordered "crystalline" portions of cellulose must be supposed to be less reactive than the disordered "amorphous" portions, which are more easily accessible to chemical reagents. Structure may affect both the rate of depolymerisation and the nature of the processes involved, by changing the relative reactivities of atoms and groups in the repeating unit.

Few data are available on the effect of the supermolecular structure on alkaline degradation, but they are consistent with the above view. Thus Meller [133] noted the effect of the structure of the cellulose fibre on the rate of the changes occurring from the reducing end, and suggested [4,133] that intramolecular and intermolecular hydrogen bonds play a part in the reactivity of celluloses.

Colbran and Davidson [12] showed that hydrocelluloses obtained from mercerised cotton cellulose are more stable to the action of hot dilute alkalis than are those obtained from unmercerised cotton cellulose of the same reducing power. The alkali-insoluble cellulose had considerably lower copper numbers and contained a greater quantity of carboxy-groups in the case of degradation of the hydrocelluloses obtained from mercerised cellulose.

The difference was explained by the effect of the supermolecular structure on the stabilising reaction, which is evidently favoured by the structure of cellulose II. Evidence of the greater resistance of this form to hot dilute alkalis is provided also by Machell and Richards' results [134] showing that pretreatment of hydrocellulose with 5 *N* sodium hydroxide solution increases its stability to the subsequent action of the 0.5 *N* alkalis at 100°C and by the enhanced stability [135] of unbleached sulphite pulp to the action of hot dilute alkalis resulting from its mercerisation.

Swelling and "decrystallisation" of cellulose diminish its resistance to hot dilute alkalis [133].

Machell and Richards [134] and Colbran and Davidson [12] observed that only certain molecules in the residue resistant to further degradation, obtained when hydrocellulose was treated with hot dilute alkali, contained metasaccharinic acid as terminal unit. These workers assumed that degradation ceased not only when the reducing terminal unit of cellulose was converted into a metasaccharinic acid residue but also when the reactant end of the molecule reached inaccessible (crystalline) regions of the cellulose fibre. Richtzenhain et al. [10] found no significant differences in the X-ray patterns or in the distribution curves for the degree of polymerisation of hydrocellulose before and after treatment with hot dilute alkali. The explanation offered was that only that part of the material located in disordered regions and on the surface of ordered regions of the cellulose suffered breakdown.

Very few results have been published on the effect of the supermolecular structure of cellulose on its oxidation by molecular oxygen in alkaline media. However, the available data indicate that the less ordered portions of cellulose are the more reactive. Thus the rate of oxidation of alkaline cellulose is considerably increased if the cellulose has first been swollen in alkali [83,99]. The X-ray patterns of cellulose oxidised after swelling are typical of cellulose hydrate, whereas the interference pattern obtained after oxidation without preliminary swelling is identical with that of native cellulose [99]. Preswelling obviously increases the proportion of amorphous regions in the supermolecular structure. As Brassard suggested [100], this process may be responsible for the increase in the rate of oxidation of alkaline cellulose with increase in the caustic soda concentration (see Section III, 1*b*).

A fairly recent investigation [136] of the effect of the supermolecular structure of cellulose on its oxidative degradation by the action of molecular oxygen on a suspension in 1% caustic soda solution at 100°C has shown a marked difference in rate of oxidation between natural cotton cellulose and cellulose hydrate obtained from cotton cellulose. After the carbonyl groups had been reduced, the hydrate was degraded at a greater rate, whereas natural cotton cellulose underwent only slight degradation. The structure of cellulose hydrate differs from that of natural cotton cellulose in the type of packing of molecules in the ordered ("crystalline") regions, in the size of the densely packed regions, and in the degree of ordering (crystallinity) of the cellulose. The influence of these structural features on the rate of oxidative-alkaline degradation was investigated.

This work showed that, after the carbonyl groups had been reduced, oxidative-alkaline degradation occurred at the same rate in densely packed regions of native cotton cellulose and in the cellulose hydrates isolated from them by hydrolysis. Thus the difference in the rates of oxidation of the two materials can be explained only by different degrees of ordering, which was confirmed by examining the oxidation of specimens of cellulose differing in this parameter. It should be mentioned in this connection that cellulose undergoes oxidation even in the absence of carbonyl groups [136]. Cellulose hydrate, which X-ray examination showed to possess a lower degree of ordering, is then oxidised especially intensely. It was concluded from the experimental results that the oxidising process can be initiated not only by carbonyl groups but also by hydroxyls situated in disordered regions.

The constancy of the degree of polymerisation during the oxidation of hydrocelluloses, obtained both from native cotton cellulose and from cellulose hydrate, implies [136] that the oxidative-alkaline degradation of hydrocelluloses takes place only from the ends of macromolecules and on the surface of ordered regions.

The above survey of the literature shows that processes involved in the degradation of the cellulose molecule and oxidised celluloses have been studied in detail, whereas the reaction mechanism of the oxidation of cellulose by molecular oxygen in an alkaline medium had not yet been adequately elucidated. These processes are of the utmost importance in the technology of cellulose and other polysaccharides, and further research is needed in order to control them.

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Zelinskii Institute of Organic Chemistry,
USSR Academy of Sciences,
Moscow