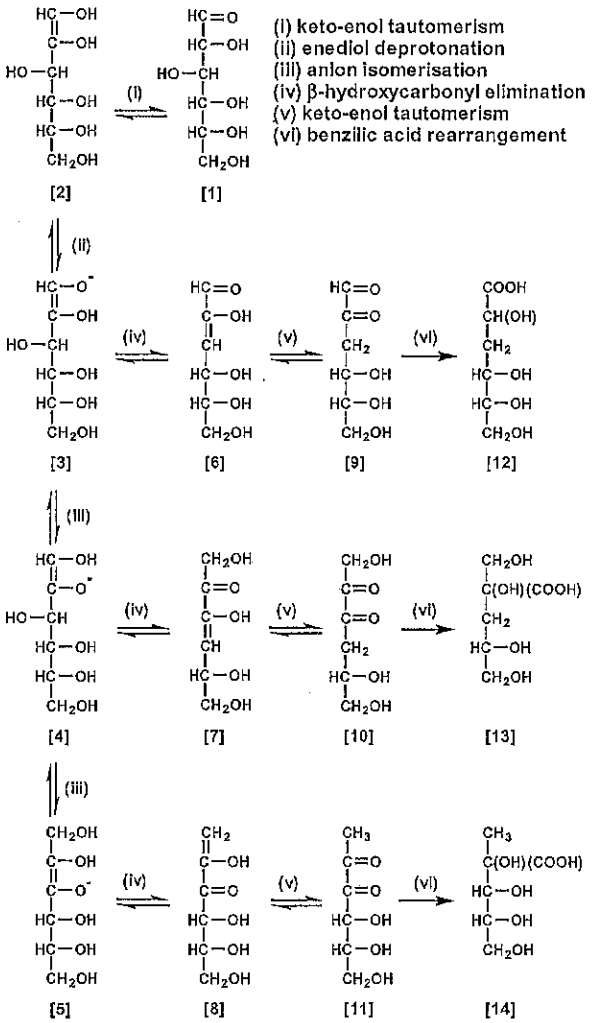

Fig. 1. Nef–Isbell mechanism for the alkaline degradation of D-glucose (**1**).

alkaline degradation of hexoses results in reaction products consisting principally of numerous acids ($\leq C_6$), e.g. the six-carbon deoxyaldonic acids (saccharinic acids) (Sowden, 1957). Higher molecular weight compounds ($>C_6$ acids), and miscellaneous non-acidic and cyclic unsaturated carbonyl compounds are also formed in minor amounts (Forsskåhl, Popoff, & Theander, 1976; Theander & Nelson, 1988). The mechanisms by which the numerous alkaline degradation products are formed are beyond the scope of this review, however, the reader is pointed in the direction of several articles that provide information on this area (Greenfield et al., 1994; Machell & Richards, 1960a,b; MacLeod & Schroeder, 1982; Sowden, 1957; Speck, 1958).

The relative composition of the alkaline degradation products is influenced by several reaction parameters, e.g. temperature, the nature and concentration of the alkali, and the monosaccharide substrates present (de Bruijn et al., 1986; de Bruijn, Kieboom, & van Bekkum, 1987a,b; de Wit, Kieboom, & van Bekkum, 1979). In summary: (i) an increase of hydroxyl ion concentration and the use of divalent cations favours the formation of 2-hydroxypropanoic acid (lactic acid) and decreases the amount of methanoic acid (formic acid), 2,3-dihydroxypropanoic acid (glyceric acid) and the total amount of C_4–C_6 acid products; (ii) the composition of reaction products is the same at either 5 or 80 °C, i.e. is independent of temperature; (iii) alkaline degradation of dilute solutions (1 mM) results in almost complete conversion of the monosaccharides into $\leq C_6$ acids; (iv) higher molecular weight compounds are found to be increased at pH 11–12 and at higher monosaccharide concentration (0.1 M).

Yang and Montgomery (1996) identified the alkaline degradation products arising from the incubation of D-glucose with calcium hydroxide at equimolar ratios at different concentrations (1.8–50% w/w, 30 min, 100 °C). In their studies, D-glucose (0.1 M) in aqueous calcium hydroxide (0.1 M) was completely degraded after 30 min at 100 °C. The principal detected products were 2-hydroxypropanoic acid (lactic acid) and the saccharinic acids, together with their lactones. The same saccharinic acids were produced at all initial concentrations of reactants. Increasing the glucose concentration generally decreased the formation of $<C_6$ acids, hydroxyethanoic acid (glycolic acid, C_2) to hydroxypentanoic acids (deoxypentonic acids, C_5), whereas the C_6 acids (glucosaccharrinic, glucoisosaccharinic and glucometasaccharinic acids) initially increased and then decreased. The C_3 acids, especially 2-hydroxypropanoic (lactic) acid, were found to be the principal components of the reaction products (41%) at lower reaction concentration whereas C_6 acids, such as 2-*C*-methylpentonic (glucosaccharrinic) acids (27%) and the 3-deoxyhexonic (glucometasaccharinic) acids (25%) were found to be major components at higher reactant concentrations. The higher concentrations of glucose appeared to decrease the secondary reactions noted in the more dilute solutions (i.e. diketo-cleavage and aldol condensation). The presence of calcium catalyses the benzilic acid rearrangement, thereby favouring the formation of 3-deoxy-2-*C*-(hydroxymethyl)-pentonic (glucoisosaccharinic) acids, consequently reducing the relative yields of other products, whereas, in the case of sodium hydroxide, considerable fragmentation to 3,4-dihydroxybutanoic (2-deoxytetronic), hydroxyethanoic (glycollic), and methanoic (formic) acids occurs (Machell & Richards, 1960a,b).

3. Alkaline degradation of substituted monosaccharides

The application of the reactions detailed in the Nef–Isbell mechanism to polysaccharides was greatly advanced by the studies of Kenner and co-workers on the alkaline degradation of *O*-substituted derivatives of simple sugars (Corbett, 1959; Corbett, Kenner, & Richards, 1955; Kenner & Richards, 1955, 1957; Richards, 1971). The alkaline degradation of 3-*O*-methyl-D-glucose (**15**) and 4-*O*-methyl-D-glucose (**18**) are

displayed in Figs. 2 and 3, respectively. As in the case for the degradation of glucose, the first stage is the formation of the respective enediols (**16** and **19**) via keto–enol tautomerism (i), which is then followed by enediol deprotonation by hydroxide ions (ii) to produce the corresponding enediol anions (**17** and **20**). In the case of the 3-*O*-methyl-D-glucose degradation pathway (Fig. 2), β-elimination (iv) then occurs. However, in the alkaline degradation of D-glucose, β-hydroxycarbonyl elimination takes place, whereas β-alkoxycarbonyl elimination takes place in the alkaline degradation of 3-*O*-methyl-D-glucose, i.e. the methoxide ion rather than the hydroxide ion is eliminated. Thus, the alkaline degradation of 3-*O*-methyl-D-glucose produces a diketodeoxyglycitol product that is also present in the alkaline degradation of D-glucose (**6**). The degradation pathway then continues as for D-glucose (Fig. 1), i.e. β-alkoxycarbonyl elimination is followed by keto–enol tautomerism (v) and benzilic acid rearrangement (vi), resulting in the formation of a mixture of 3-deoxy-D-arabino-hexonic and 3-deoxy-D-ribo-hexonic acids (D-glucometasaccharinic acids) (**12**) (Fig. 2).

The alkaline degradation of 4-*O*-methyl-D-glucose (Fig. 3) is slightly different. β-alkoxycarbonyl elimination of the enediol anion (**20**) cannot take place straight away since the methoxyl group is not in the β-position relative to the negative charge of the anion, it is in fact in the γ-position. However, after sufficient time has elapsed 4-*O*-methyl-D-fructose is produced via the Lobry de Bruyn/Alberda van Ekenstein transformation (i.e. isomerisation (iii) of anion (**20**) to (**21**) followed by reprotonation). Anion (**21**) has the methoxyl group in the β-position relative to the negative charge of the anion and thus β-alkoxycarbonyl elimination of the enediol anion (**21**) takes place. Therefore, β-alkoxycarbonyl elimination produces a diketodeoxyglycitol product that is also present in the alkaline degradation of D-glucose (**7**). The degradation pathway then continues as for D-glucose (Fig. 1), i.e. keto–enol tautomerism (v) of (**7**) produces 4-deoxy-D-glycero-2,3-hexodiulose (**10**) and subsequent benzilic acid rearrangement (vi) of (**10**) results in the formation of a mixture of 3-deoxy-2-*C*-(hydroxymethyl)-D-threo-pentonic and 3-deoxy-2-*C*-(hydroxymethyl)-D-erythro-pentonic acids (D-glucoisosaccharinic acids) (**13**) (Fig. 3) (Kenner & Richards, 1955).

β-Alkoxycarbonyl elimination occurs more readily than β-hydroxycarbonyl elimination since it is an irreversible reaction whereas all of the others displayed in Figs. 1–3, with the exception of the benzilic acid rearrangement (vi), are reversible and are thus subject to the law of mass action, which inhibits hydroxyl elimination but has no such effect on methoxyl elimination (Kenner & Richards, 1957).

The identity of the saccharinic acids produced upon alkaline degradation can thus be used to provide distinction between 3-*O*- and 4-*O*-substituted sugars (Blears, Machell, & Richards, 1957; Kenner, 1955), and can be applied for studying the alkaline degradation of oligosaccharides and polysaccharides (Burns & Somers, 1973; Whistler & BeMiller, 1958). The formation of 3-deoxy-2-*C*-(hydroxymethyl)-D-erythro- and threo-pentonic acids (D-glucoisosaccharinic acids) is favoured for the alkaline degradation of 4-*O*-substituted glucose derivatives (e.g. 4-*O*-methyl-D-glucose, maltose, amylose and cellulose) with calcium hydroxide, whereas in the case of sodium hydroxide, fragmentation predominates (Machell & Richards, 1960a,b).

4. Cellulose degradation

4.1. End-wise degradation (peeling)

At temperatures $<170\,^{\circ}C$ the glycosidic $(1 \rightarrow 4)$-linkages between the β-D-Glc*p* units in cellulose are alkali stable. However, a significant reduction in molecular weight is observed when cellulose is boiled with dilute sodium hydroxide at such temperatures, even with the careful exclusion of oxygen, a problem that was observed many years ago with respect to the scouring of cotton for textile purposes (Fargher & Higginbotham, 1924). Davidson (1934) suggested that the losses were caused by the dissolution of short-chain material detached from the reducing ends of the cellulose molecules (known generally as 'peeling' or 'unzipping'). The predominant mechanism of cellulose degradation was shown to be the formation of the 3-deoxy-2-*C*-(hydroxymethyl)-erythro- and threo-pentonic acids (D-glucoisosaccharinic acids) (**13**) (Colbran & Davidson, 1961; Machell & Richards, 1960a,b; Nevell, 1985a; Richards, 1963; Richards & Sephton, 1957), as in the alkaline degradation of 4-*O*-methyl-D-glucose (Fig. 3). However, in the case of cellulose degradation, β-alkoxycarbonyl elimination (vii) is the elimination of the rest of the cellulose chain to release D-glucoisosaccharinic acids (i.e. the R group in Fig. 3 represents the rest of the β-D-$(1 \rightarrow 4)$-

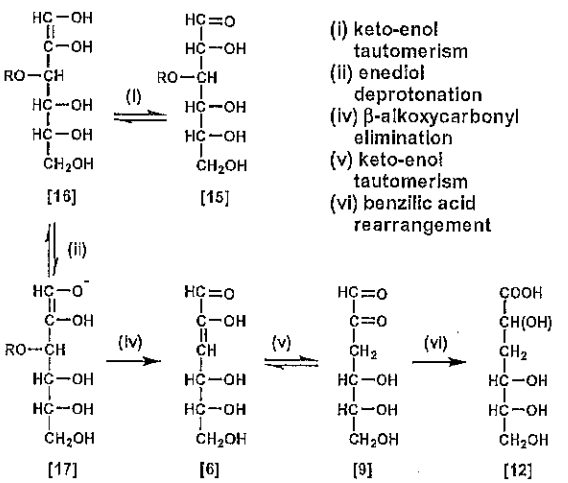

Fig. 2. Alkaline degradation of 3-*O*-substituted D-glucose (**15**).

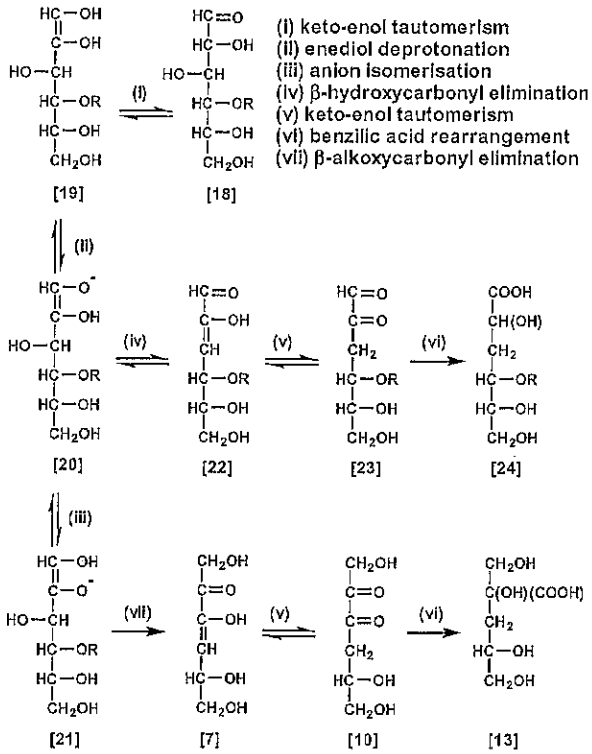

Fig. 3. Alkaline degradation of 4-*O*-substituted D-glucose (18).

Glc*p* chain). This generates a new deprotonated end group, which undergoes further alkaline degradation, and so on.

The presence of calcium ions improves the yield of (**13**) by catalysing its production from 4-deoxy-D-glycero-2,3-hexodiulose (**10**). Ziderman (1980) found that alkaline earth metal ions result in a higher weight loss (due to peeling) and consequent greater acid production compared with alkali metal ions, at low alkali concentrations (~0.02 M).

4.2. Termination (stopping)

If the erosion of cellulose molecules from their reducing ends (peeling) were to continue unchecked, the whole of the cellulosic material would eventually dissolve (Nevell, 1985a). However, it is well known that this is not the case, since otherwise the scouring of cotton textiles and the Kraft process for wood pulping would not be possible. Stabilisation of the cellulose is achieved by a competing reaction (a 'stopping' reaction) (Machell & Richards, 1957, 1960b). If one looks at the degradation of a 4-*O*-substituted glucose (Fig. 3), e.g. a cellulose reducing end group, one can see that β-hydroxycarbonyl elimination (iv) can occur. Although, as previously mentioned, β-alkoxycarbonyl elimination (vii) occurs more readily, a significant proportion of β-hydroxycarbonyl elimination (iv) also occurs, resulting in the formation of terminal 4-*O*-substituted 3-deoxy-D-arabino- and ribo-hexonic acid units (**24**), i.e. substituted D-glucometasaccharinic acids (**12**). Besides the 3-deoxyhexonic acid units, 16 other stabilising acid terminal units have been detected in alkali-boiled hydrocellulose (Johansson & Samuelson, 1974, 1975, 1978). The principle behind the stopping reaction can be purposely applied by modifying cellulose end groups in order to produce alkali stable cellulose derivatives (Procter & Wiekenkamp, 1969).

Some reducing end groups can remain in a fully alkali-stabilised hydrocellulose because of their inaccessibility with respect to the alkali (see Section 4.5), due to the physical nature of the cellulosic material (Corbett, 1959, 1960; Haas, Hrutfiord, & Sarkanen, 1967). The concentration of alkali is important with respect to this (Lai & Ontto, 1979). Thus, even with high weight losses due to alkaline hydrolysis (e.g. up to 50%), observed average degree of polymerisation (DP) remains constant (Davidson, 1934) or even increases slightly (Johansson & Samuelson, 1975; Machell & Richards, 1957). Any increase must be due to dissolution of short-chain material in hot alkali.

4.3. Alkaline scission

When cellulose is heated at >170 °C random alkaline scission (hydrolysis) of glycosidic linkages occurs resulting in considerable weight loss and marked decrease in DP (Nevell, 1985a). Scission does not appear to depend on the presence of molecular oxygen and is followed by peeling from any new reducing end group produced by the scission process thereby resulting in much greater weight losses than alkaline degradation at lower temperatures (Richards, 1963, 1971). However, at such higher temperatures end group stabilisation (stopping) has a greater effect than at lower temperatures (Nevell, 1985a).

The glycosidic linkages may be cleaved either between the oxygen atom and the glucosyl group or between the oxygen atom and the aglycone. Both reactions occur, however cleavage of the oxygen–glucosyl bond predominates. A more in depth discussion of the mechanism of alkaline scission can be found in Nevell (1985a). Although alkaline scission is normally only associated with alkaline degradation at higher temperatures, it has been observed in the alkaline degradation of amorphous hydrocellulose at temperatures <100 °C (Gentile, Schroeder, & Atalla, 1987).

4.4. Aerobic (oxidative) alkaline degradation

Although anaerobic conditions will prevail in the long term, there will be a short period of time during and shortly after resaturation when aerobic conditions are present. The oxidation of alkali cellulose by atmospheric molecular oxygen has long been used for the reduction of the DP of wood pulp (the aging or preripening process) to a level suitable for the manufacture of viscose rayon (Treiber, 1985). The first step in this autoxidation process results in the formation of carbonyl-containing oxidised celluloses (oxycelluloses), which are subsequently degraded by alkali