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Note

The resistance of ketocelluloses to chain end-initiated depolymerisation during alkali-catalysed chain-scission*

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The amount of yellow chromogen in alkaline extracts of celluloses and starches provides a quantitative estimate of the extent of chain end-initiated depolymerisation ("peeling" reaction) that has occurred by β-elimination[1–3]. However, the results are more difficult to evaluate when concurrent cleavage of non-terminal glucosidic linkages occurs. Ketocelluloses are largely resistant to extraction with dilute aqueous alkali, and the extract is not coloured[1,4]. A mechanistic explanation for this stability is now presented.

When cotton cellulose is treated with bromine water to an oxidant consumption of ~60 mequiv./100 g, an oxycellulose containing 12 ketone groups per molecule of d.p. 1170 (Table I, substrate 2) is obtained[4]. On alkaline extraction of this substrate, the yellow colour produced per aldehyde group (*i.e.*, per reducing end-group) is equal to that obtained during the degradation of hydrocellulose (Table I, substrate 1) under the same reaction conditions.

TABLE I

YELLOW COLOURATION OF ALKALINE EXTRACTS OF CELLULOSES

Cellulose substrate			*Functional groups per molecule*			*Yellowing*[d] *(per aldehyde group)*	*Ref.*
No.	*Pretreatment*	*D.p.w*	*Ketone*	*Aldehyde*	*Carboxyl*		
1	Hydrochloric acid[a]	160–2500	0	1	0	0.071	4
2	Bromine water[b]	1170	12	0.59	2.1	0.073	4
3	Hydrogen peroxide[c]	2270	8	0.73	6.7	0.050	5
4	Hydrogen peroxide[c]	1160	17	0.53	4.5	0.054	5
5	Hydrogen peroxide[c]	2150	20	0.73	6.4	0.057	5

[a]5M, 25°, various times. [b]12mM, pH 2, 25°. [c]0.3M, pH 9.6, 80°. [d]Colour of supernatant solution after the substrate had been treated for 1 h in boiling, aqueous sodium hydrogencarbonate (0.6M); measured with a colorimeter.

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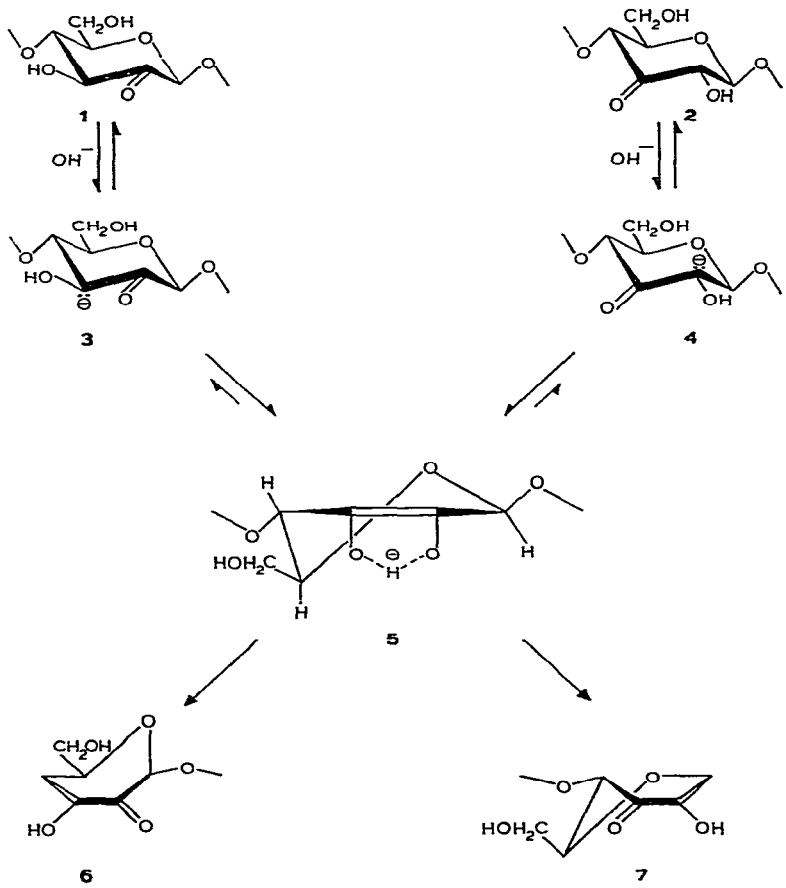
The very weak, yellow colour generated from the ketocellulose may therefore be accounted for, quantitatively, solely by "peeling" from those reducing termini initially present in the substrate[4]; the ketone groups do not contribute to the yellowing. A similar result is obtained[5] with hydrogen peroxide-oxidised celluloses (Table I, substrates 3–5). Achwal and Shenker[6] detected the formation of α-hydroxymonoketo groups during the oxidation of cotton cellulose with chlorous acid, but no enhanced yellowing or dissolution was found[7] on alkaline extraction of this ketocellulose.

Ketone groups in oxycelluloses may be located at C-2 or C-3. The alkali-catalysed, chain-scission reaction has been studied by using monosaccharide model compounds in which all of the hydroxyl groups are etherified. Thus, methyl 4-*O*-ethyl-3-*O*-methyl-β-D-*threo*-pentopyranosid-2-ulose loses EtO-4 by β-elimination, forming methyl 4-deoxy-3-*O*-methylpent-3-enopyranosid-2-ulose[8]. Methyl 2,4,6-tri-*O*-methyl-D-*ribo*-hexopyranosid-3-ulose anomers eliminate MeO-1, yielding 1,5-anhydro-2,4,6-tri-*O*-methyl-D-*erythro*-hex-1-en-3-ulose[9]. Accordingly, Lewin and Ettinger[5] pointed out that a 2-ketocellulose (**1**) could undergo chain breakage with subsequent "peeling" of the HO-1-terminated fragment released from C-4, whereas



a 3-ketocellulose (**2**) would yield alkali-stable fragments, as was found experimentally with the ketocelluloses described above. The available evidence suggests that scission would not occur at postulated 2,3-diketonic D-glucose residues[10–12].

A 2-ketocellulose[13] of d.p. ~225, containing ~170 carbonyl groups per molecule, decomposed[14] in water (pH 6.5, room temperature, 30 min) with a 40% weight-loss, yielding a product of d.p. ~160. On treatment with 0.1M sodium hydroxide, a 60% loss in weight occurred[14], leaving a residue of d.p. ~50, but the yellow colour was weak, in contrast to the strong yellow colour of 6-aldehydo-cellulose[13].

Identification of products[15], and p.m.r. studies[16] of alkali-treated methyl D-*arabino*-hexopyranosid-2-uloses and D-*ribo*-hexopyranosid-3-uloses have confirmed the postulate[17] that ketocelluloses **1** and **2** will both be readily converted, *via* the respective carbanions **3** and **4**, into a common, tautomeric 2,3-enediolate anion **5** in dilute alkali. Intermediate **5** presumably adopts the half-chair conformation $^{O}H_{5}$ depicted, where the orientation of the O-5,C-5,C-6 half of the ring present in the parent conformations **1–4** is retained. Chain cleavage may now occur by two competitive routes. Elimination of O-1 from **5** will leave a chain fragment terminated by the enone moiety **7**, while the second fragment will bear a new, non-reducing chain-terminus. Neither fragment would undergo alkaline "peeling". Alternatively, O-4 may be cleaved from **5**, leaving a chain bearing the enone moiety **6**, and liberating a chain fragment terminated by a new reducing moiety, which will initiate "peeling" with concomitant dissolution and formation of a yellow colour. Dreiding models of intermediates **6** and **7** show that five ring-atoms are held coplanar by the conjugated enone system, the single exoplanar atom giving the "sofa" conformations[18] depicted, with O-5 above or C-5 below the plane of the ring, respectively.

Their resistance[1,4,5,7,13] to depolymerisation indicates that the former route (**5**–**7**) is the preferred mode of alkali-catalysed chain-scission in ketocelluloses. Consideration was given to three factors that may contribute to this preference: stereochemical, electronic, and kinetic.

First, for **1** and **2**, the eliminations follow a syn (axial–equatorial) stereochemistry. Furthermore, intermediates **6** and **7** are both formed by the expulsion of a quasi-equatorial, allylic oxygen atom from **5**. It therefore appears that stereochemical factors may not be adduced to rationalise an enhanced rate of formation of **7**.

Second, calculation of the electronic distribution in pyranoses has demonstrated[19] that the negative charge decreases in the order: O-1*e* > O-4*e* = O-1*a* > O-5, while the greatest positive charge residues on C-1. For β-D-glucopyranose in the $^{4}C_{1}$ conformation, the following charges were obtained[19]: O-1, −0.2872; O-4, −0.2610; and O-5, −0.2538. The use of these results in order to rationalise the chemistry of pyranosides[19] implies that the electronic distributions calculated for the pyranoses retain their validity for ether derivatives. Accordingly, it may be concluded that a charge distribution in **5** similar to that detailed above would render O-1 a better leaving-group than O-4, thus facilitating the formation of **7** rather than **6**. Furthermore, no competitive elimination of the third allylic oxygen atom (O-5) is indicated.

Third, in contrast to the situation in **7**, intermediate **6** is destabilised by the

anomeric effect (O-1*e*). Furthermore, a small syn-axial interaction may exist in **6** between H-1 and H-5, which are separated by only 2.25 Å in the Dreiding model, as compared to 2.4 Å for the combined van der Waals radii[20] of two hydrogens. Both these contributions to the free energy of **6** are absent from **7**. Therefore, if the transition state in the transformations **5**→**6** and **5**→**7** is similar in structure to the product, a lower activation energy is expected for the formation of **7**, which will accordingly be the major product from **5** due to this kinetic control.

The transformation depicted in the Scheme is an ElcB mechanism, in which all of the substrate (**1** or **2**) is rapidly converted, *via* the conjugate base (**3** or **4**, respectively), into a stabilised intermediate **5**, which decomposes to products in a rate-determining, unimolecular, elimination step[21]. A fully analogous mechanism is accepted[22] for chain cleavage in 1,4-(polyglycosiduronates) by β-elimination from C-4.

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