909. *Alkaline Degradation of Polysaccharides. Part V.* Periodate Oxycellulose.†*

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Earlier work on the alkaline degradation of simple analogues has been extended to periodate oxycellulose. Identification of glycollic and αγ-di-hydroxybutyric acid as the predominant soluble acidic products is interpreted as evidence that the original scission of the polymer occurs mainly by β-alkoxycarbonyl elimination at the $C_{(5)}$–O group of the origina lanhydroglucose unit. There is also some evidence that a Cannizzaro rearrangement may occur, with formation of acidic polysaccharides.

THE degradation of carbonyl oxycelluloses is of considerable technological importance since it is responsible for the tendering of oxidised cellulose fabrics during scouring, laundering, or similar mild alkaline treatments. Since periodate oxycellulose is the only type of oxidised cellulose available which approaches chemical uniformity it is the most suitable material for this work. Previous studies [1-3] of the alkaline degradation of periodate oxycellulose have yielded no conclusive evidence of the mechanism of degradation. Several types of interpretation have been advanced [1-9] for the rapid depolymerisation which is known [1] to occur under mild alkaline conditions, but two theories in particular have predominated. First, Pacsu [3] likened the structure of the enol of periodate oxycellulose to a hydroxy-keten acetal and so interpreted the alkaline scission reaction as a hydroxy-keten acetal hydrolysis, yielding, ultimately, erythrose and glycollic acid from an oxidised anhydroglucose unit. This theory, as proposed, is inconsistent with Head's isolation [2] of glyoxal from the alkaline degradation of both periodate oxycellulose and periodate-oxidised methyl β-D-cellobioside. Secondly, Haskins and Hogsed [5] applied Isbell's β-hydroxycarbonyl-elimination mechanism [10] to periodate oxycellulose and suggested that scission of the $C_{(5)}$–O bond, by this mechanism would result in the formation of glyoxal and a tetrose, the tetrose arising from structures such as (II). However, while results with model compounds [9] recently confirmed the view that β-alkoxycarbonyl elimination from position 5 of the original anhydroglucose unit is the most likely cause of alkaline scission in periodate oxycellulose, the subsequent reactions differed from those postulated by Haskins and Hogsed. The present work was undertaken to test these conclusions by a study of the oxycellulose itself.

Preliminary study of four periodate oxycelluloses of different degrees of oxidation (0·24, 0·40, 0·80 and 1·01 moles of periodate/anhydro-glucose unit) showed that degradation in oxygen-free lime-water at room temperature was rapid, the oxycelluloses disintegrating to a powder and soluble acids being produced. The presence of glycollic acid and αγ-dihydroxybutyric acid was indicated by paper chromatography and confirmed by isolation of crystalline derivatives. The formation of volatile acids was also demonstrated.

Quantitative studies were carried out on two oxycelluloses (0·24 and 0·80 mole of periodate/anhydro-glucose unit). It was not possible to determine the rate of consumption

[1] Davidson, *J. Textile Inst.*, 1938, **29**, T195; 1940, **31**, T81; 1941, **32**, T109.

[2] Head, *ibid.*, 1947, **38**, T389.

[3] Pacsu, *Textile Res. J.*, 1945, **15**, 354.

[4] Kaverzneva, Ivanov, and Solova, *Bull. Acad. Sci. U.S.S.R.*, 1952, 681.

[5] Haskins and Hogsed, *J. Org. Chem.*, 1950, **15**, 1264.

[6] Corbett, Kenner, and Richards, *Chem. and Ind.*, 1953, 154.

[7] Kenner, *Chem. and Ind.*, 1955, 727.

[8] Corbett and Kenner, *J.*, 1953, 2245.

[9] O'Meara and Richards, *J.*, 1958, 1204.

[10] Isbell, *J. Res. Nat. Bur. Stand.*, 1944, **32**, 45.

of alkali directly because of sorption of cations by the oxycellulose in the initial stages of the reaction. As degradation proceeded some of the alkali redissolved. The reaction was therefore studied in two stages, first the initial reaction up to $1\frac{1}{2}$ hr., at the end of which the solid residue was separated, and secondly, the final reaction involving the degradation by alkali to stability of the soluble neutral products from the initial reaction. At each stage the soluble products were separated into neutral and acidic components, and the acids were estimated and identified by methods described previously.[9]

The acids were divided into volatile and non-volatile fractions. The former were mainly formic acid, and the latter glycollic acid, $\alpha\gamma$-dihydroxybutyric acid, and other acids which on paper chromatography had low mobility (R_F 0—0·20) and may include the products of Cannizzaro rearrangements of oxidised anhydroglucose units, such as were detected with model compounds.[9] The results are summarised in the Table.

Degradation of periodate oxycelluloses in 0·045N-*lime-water at* 20°.

	Yield (per g. of oxycellulose)					
	A			B		
Products	Initial	Final	Overall	Initial	Final	Overall
Insoluble residue (g.)	0·67	—	0·67	0·13	—	0·13
Neutral products (g.)	0·25	0·06	0·06	0·39	0·06	0·06
Acidic products (milliequiv.)						
Formic acid	0·12	0·10	0·22	0·43	0·20	0·63
Other volatile acids	0·05	0·05	0·10	0·11	0·10	0·21
Glycollic acid	0·40	0·26	0·66 (53%) †	0·97	0·90	1·87 (46%) †
$\alpha\gamma$-Dihydroxybutyric acid	0·19	0·10 ^{a}	0·29 (23%) †	0·68	0·51	1·19 (29%) †
Acids of low mobility *	0·08	0·11	0·19	0·78	0·40	1·18
Total acids	0·84	0·62	1·46	2·97	2·11	5·08

A, B: Periodate oxycelluloses, IO_4^-/anhydro-glucose unit, 0·24 and 0·80 respectively.
^{a} Includes other acids and lactones not separately identified.
* R_F, 0—0·20, solvent *a*.
† Percentage of theoretical maximum yield, after allowance for losses in paper chromatography.

From these results it is clear that the extent of degradation depends on the original degree of oxidation, and the low final yield of neutral products shows that degradation proceeds almost completely to give acids amongst which glycollic and $\alpha\gamma$-dihydroxybutyric predominate. The products of low chromatographic mobility formed a smaller proportion of the soluble acids from the less highly oxidised cellulose. This may be partly due to the fact that at low degrees of oxidation the products of Cannizzaro rearrangement, whose formation does not involve chain scission, are increasingly included in the insoluble residue, which was in fact shown to contain acidic groups.

On the basis of the mechanisms of alkaline degradation of periodate oxycellulose put forward by Pacsu [3] and Head [2] erythrose was predicted as one of the primary products, the other product being either glycollic acid (Pacsu [3]) or glyoxal (Head [2]). Head pointed out that except under very mildly alkaline conditions glyoxal would be rapidly converted into glycollic acid and thus, under the conditions used in the present work, both of these mechanisms predict glycollic acid and erythrose as degradation products. Similarly in the view of Haskins and Hogsed [5] the expected products would be glycollic acid and a tetrose. However, it has been shown that the main products resulting from chain-scission of periodate oxycellulose are glycollic and $\alpha\gamma$-dihydroxybutyric acid, and since alkaline degradation of erythrose does not give high yields of $\alpha\gamma$-dihydroxybutyric acid [11] this is not in accord with any of the above hypotheses.

By analogy with the simple model compounds previously studied [9] these results may however be interpreted as shown (I $\longrightarrow$ II, etc.). Neglecting end-units the three possible types of primary product, resulting from β-alkoxycarbonyl elimination in any partially oxidised periodate oxycellulose are (II), (III), and (IV). The results of work with model compounds [9] and also an investigation of the properties of glyoxal hemiacetals [11] suggest

[11] O'Meara, unpublished results.
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that an intermediate of type (III) will readily break down in lime-water at room temperature as shown, yielding equivalent amounts of glycollic and $\alpha\gamma$-dihydroxybutyric acids. The intermediate (IV) would similarly be expected to break down readily as shown to yield glycollic acid and a normal, non-reducing glucose end unit. In the case of an intermediate of type (II) however, the α-alkoxycarbonyl group would not be expected to undergo further rapid alkaline degradation under these conditions [12] and compound (II) would therefore
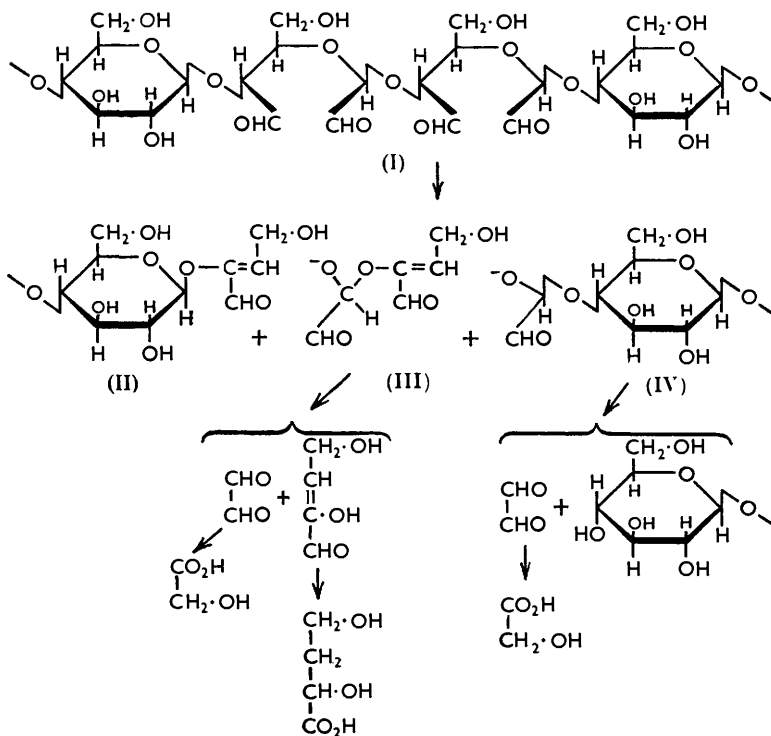
accumulate and possibly ultimately degrade by other mechanisms. The lower yield of $\alpha\gamma$-dihydroxybutyric than of glycollic acid may be partly explained on this basis, particularly since the relative proportion of the $\alpha\gamma$-dihydroxybutyric acid is greater at higher extent of oxidation, contribution from intermediates of type (II) being then reduced. However, the yields of both glycollic and $\alpha\gamma$-dihydroxybutyric acid are very much lower than theoretical and although the reactions shown may be regarded as the predominant mechanism of alkaline scission of periodate oxycellulose, alternative mechanisms, which would produce the same type of depolymerisation, cannot be excluded on the present evidence. In particular Pacsu's keten acetal mechanism [3] is of interest since contribution from this type of reaction would also explain the excess of glycollic over dihydroxybutyric acid.

No explanation for the formation of formic acid is offered.

EXPERIMENTAL

The following solvents and sprays were used for paper chromatography (cf. ref. 9) on Whatman No. 1 paper at 25°: solvents; *a*, ethyl acetate–acetic acid–water (10 : 1·3 : 1), *b*, butan-1-ol–pyridine–benzene–water (4 : 2 : 1 : 1). Sprays; *a*, " B.D.H " 4·5 indicator; *b*, permanganate–periodate; *c*, silver nitrate–sodium hydroxide.

Total acids, volatile acids, and glycollic acid were determined as described previously.[9]

[12] Kenner and Richards, *J.*, 1956, 2921.

Preparation of Periodate Oxidised Cellulose.—Chemically untreated Sudan-Sakel cotton in in the form of carded sliver was boiled gently with 2% aqueous sodium hydroxide (40 ml./g.) for 16 hr., filtered off, washed with water until free from alkali, then with acetone, alcohol, and ether, and dried *in vacuo* at 20°. The dry, scoured cotton was oxidised by 0·1M-sodium metaperiodate (100 ml./g.), reaction being followed by titration of an aliquot portion (1·0 ml.) with sodium thiosulphate.[9] When the desired degree of oxidation had taken place, the oxycellulose was washed thoroughly and dried as above.

Alkaline Degradation of Periodate Oxycellulose.—(i) *Periodate-oxidised cellulose* (oxidised: 0·80 *mole of periodate/anhydroglucose unit*). The oxidised cellulose (5·0 g.) was stirred with oxygen-free 0·045N-lime-water (3·0 l.). The cellulose disintegrated (*ca.* 15 min.), leaving a fine, fibrous insoluble residue. After 1½ hr., when the apparent consumption of alkali, measured by back-titration of an aliquot portion of the solution after addition of excess of acid, was 42 milliequiv., the reaction was stopped with excess of carbon dioxide. The mixture was filtered (filtrate F), the solid residue (2·51 g.) being subsequently suspended in water (50 ml.), washed free from some calcium carbonate and absorbed calcium hydroxide by dilute hydrochloric acid and then treated with lime-water to neutralise the acidic groups. The residual solid (0·65 g.) (Found: Ca, 0·8%) was filtered off, washed, and dried. The main filtrate (F), after concentration to *ca.* 600 ml. and removal of precipitated calcium carbonate, was separated into neutral and acidic components by means of the Amberlite resins IR-120(H) and IRA-400 (carbonate form) as described earlier.[9] The neutral material (N) (1·95 g.) was obtained as an amorphous powder, and the acids were obtained as a solution of their ammonium salts. An aliquot portion of the latter solution was used in the determination [9] of the total acids (14·9 milliequiv.), volatile acids (2·7 milliequiv.), and formic acid (2·15 milliequiv.), the presence of acetic acid being shown by a qualitative test.[13] Quantitative paper chromatography of a portion of the free acids [9] (1·94 milliequiv.) (solvent *a*) resulted in the isolation of glycollic acid (0·50 milliequiv.). αγ-dihydroxybutyric acid (including lactone) (0·35 milliequiv.), and acids of low mobility (R_F 0— 0·15) (0·4 milliequiv.). Thus, after allowance for guide strips and volatile acids, the recovery was 86%.

The neutral material (N) (1·95 g.) was dissolved in water (50 ml.), mixed with oxygen-free 0·04N-lime-water (1 l.), and kept until alkali uptake ceased (11 days). Excess of carbon dioxide was then added, and the mixture concentrated to *ca.* 300 ml., filtered free from calcium carbonate and by means of Amberlite resins IR-120(H) (25·0 ml.) and IRA-400 (carbonate form; 25·0 ml.) in the usual way [9] was separated into neutral components (0·30 g.) and acidic components, the latter being recovered as the ammonium salts. Quantitative examination of the acids, as described above, gave total acids (10·5 milliequiv.), volatile acids (1·5 milliequiv.), and formic acid (1·17 milliequiv.). Paper-chromatography of the free acids (1·5 milliequiv.) resulted in the isolation of glycollic acid (0·45 milliequiv.), αγ-dihydroxybutyric acid (0·25 milliequiv., including lactone), and acids of low mobility (R_F 0·15) (0·2 milliequiv.), the recovery, after allowance for volatile acids and guide strips, being 78%. At each stage the glycollic acid was characterised as its 4-bromophenacyl ester, m. p. and mixed m. p. 138—140°, and the αγ-dihydroxybutyric acid as its brucine salt, m. p. and mixed m. p. 168—170°.

(ii) *Periodate-oxidised cellulose* (oxidised: 0·24 *mole of periodate/anhydroglucose unit*). The oxycellulose (5·0 g.) was stirred with 0·04N-calcium hydroxide (1·5 l.). After 90 min. the reaction was stopped by addition of excess of carbon dioxide. The solid residue was washed with dilute hydrochloric acid and then lime-water, dried, and weighed (3·25 g.) (Found: Ca, 0·8%). The main filtrate was then separated into neutral and acidic components as described above. The neutral material was obtained as an amorphous powder (N′) (1·26 g.), and the acids as a solution of their ammonium salts. Quantitative estimation of the acids gave total acids (4·25 milliequiv.), volatile acids (0·85 milliequiv.), and formic acid (0·59 milliequiv.). By quantitative paper chromatography of a portion of the acids (1·69 milliequiv.), glycollic acid (0·65 milliequiv.), αγ-dihydroxybutyric acid (0·31 milliequiv.), and acids of low mobility (R_F 0—0·18) (0·13 milliequiv.) were isolated. Recovery was 87%. The neutral material (N′) (1·26 g.) was treated with 0·044N-calcium hydroxide (250 ml.) at room temperature until alkali stability was reached. The mixture was treated as described above and yielded a neutral syrup (0·30 g.), together with acids, quantitative estimation of which gave total acids (3·1 milliequiv.), volatile acids (0·77 milliequiv.), and formic acid (0·52 milliequiv.). Quantitative paper chromatography of a portion of the acids (1·5 milliequiv.) resulted in the isolation of

[13] Feigl, " Spot Tests in Organic Analysis," Elsevier, Amsterdam, 1956, 5th Edn., p. 342.

glycollic acid (0·40 milliequiv.), αγ-dihydroxybutyric acid contaminated with very small amounts of other acids and lactones (0·16 milliequiv.), and acids of low mobility (R_F 0—0·20) (0·17 milliequiv.).   Recovery was 73%.

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