

Characterisation of Acidic Groups in Oxycelluloses. II. Estimation of Carboxyl Groups and Lactones by Iodometric Method

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Synopsis

A differentiation between free carboxyl and various lactone groups in oxycelluloses was carried out based on the variation in their reaction rates with KI-KIO₃ solution. An attempt has been made to identify the various lactone groups present by comparison of the results of different oxycelluloses as well as study on some model compounds. A characteristic and group spectrum was determined for each oxycellulose. On blocking the free carboxyl groups by zinc acetate treatment, the results for the nature and amounts of various lactones present are in good agreement with the results for oxycelluloses themselves. Sodium borohydride treatment for 120 hr has been found to be incapable of reducing all the lactones present. An appreciable decrease in the value for glucono- δ -lactone was observed, while glucuronic acid lactone was only partially attacked. Treatment with chlorous acid resulted in an increase in the values for free carboxyl as well as lactones for all oxycelluloses.

INTRODUCTION

Among the various types of functional groups, besides free carboxyl groups, formed during oxidation of cellulose with various oxidizing agents, only lactones seem to affect the acid content values as estimated iodometrically.¹ The cleavage of lactone groups has been shown to be incomplete during 24 hr, the period normally used for carboxyl estimation, and the extent of cleavage seems to depend on the nature of the lactone present. Slavik et al.^{2,3} have described an iodometric method to characterize and estimate various lactone groups besides free carboxyls in pulps by a rate analysis study. However, a kinetic study of the estimation of acid groups in oxycelluloses by direct iodometric titration was found to be unsuitable for characterizing different types of lactones owing to some side reactions taking place causing an anomalous rise in carboxyl content after prolonged periods of contact.⁴ The side reactions are likely to be caused by the action of liberated free iodine on the oxycellulose during the interval between two titrations; the side reactions are prevented by using the indirect iodometric titration method involving addition of sodium thiosulfate along with KI-KIO₃ and estimating the excess of thiosulfate periodically. An attempt has been made to identify and estimate various

types of lactone groups in cotton oxycelluloses and their modified products by the above technique.

EXPERIMENTAL

The procedure adopted for the preparation of various oxycelluloses and their modifications by chlorous acid and sodium borohydride treatments as well as for rendering the samples cation free have been described earlier.¹

Treatment of Samples with Zinc Acetate.³ A part of each of the decationized sample was treated with a 0.1*N* zinc acetate solution for 1 hr at a liquor ratio of 50:1, followed by washing with carbon dioxide-free distilled water.

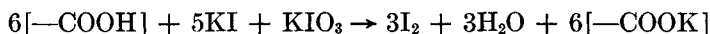
Indirect Iodometric Titration. The concentrations of the KI-KIO₃, NaCl-Na₂S₂O₃ solutions were same as in the iodometric method of Nabar and Padmanabhan.⁵ A sample, 0.5 g, was placed in a quick-fit flask, and 25 ml of the above solution was added. The flask was kept for definite periods ranging from 6 min to 120 hr and the contents titrated against a standard solution of iodine (0.01*N*) using starch as indicator. For each oxycellulose, duplicate readings were taken for each period with separate samples, along with two blanks, and the carboxyl content was calculated.

RESULTS

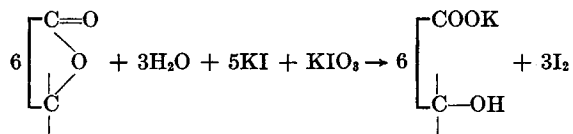
Theoretical

The basis of the present rate analysis method is that whenever there is a mixture of two or more homologous organic substances having similar functional groups but differing slightly in chemical properties, it is possible to analyze them on the basis of their differences in reactivity with a particular reagent. In the indirect iodometric titration, the following three reactions take place:

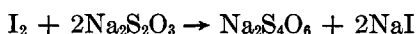
1. The free carboxyl groups react with KI-KIO₃ solution, liberating iodine:



2. The different types of lactone groups are likely to be cleaved at slower rates by KI-KIO₃ solution, liberating equivalent amount of iodine:



3. The iodine liberated by both the above reactions will be taken up by the excess of sodium thiosulfate:



According to Siggia and Hanna,⁶ many reactions in organic analysis via the functional groups are second-order reactions. The reactions of various acidic groups with KI-KIO₃ solution have been shown to be of second order by Slavik et al.^{2,3,7} from their measurements of model compounds as well as pulp samples. The method followed by Slavik et al.,² which is based on a procedure used by Sihtola et al.¹⁸ for the analysis of various carboxyl groups, has been adopted in the present work.

The general equation for the determination of the rate constant of a second-order reaction is given by

$$k = 2.303[I - K_n]t^{-1} \left(\log \left[\frac{K_n - K_{n-1}}{I - K_{n-1}} \right] + \log \left[\frac{I - K_t}{K_n - K_t} \right] \right) \quad (1)$$

where I = total milliequivalents of iodine in iodometric solution; K_n = total amount in milliequivalents of acid groups; and K_t = total amount in milliequivalents of acid groups reacted at any time t .

Simplifying eq. (1) and changing it to the form $y = mx + c$ yields

$$\log \left[\frac{I - K_t}{K_n - K_t} \right] = \frac{k(I - K_n)t}{2.303} + \log \left[\frac{I - K_{n-1}}{K_n - K_{n-1}} \right] \quad (2)$$

Hence on plotting $\log [I - K_t/K_n - K_t]$ against time t , a plot is obtained of linear nature in a definite region where the slowest reaction is taking place. Extrapolation of the linear portion intercepts the Y -axis at the point

$$I_0 = \log \left[\frac{I - K_{n-1}}{K_n - K_{n-1}} \right] \quad (3)$$

The value of K_{n-1} , i.e., the sum of the faster reacting components can then be calculated from eq. (3). The difference between K_n and K_{n-1} determines the quantity of the n th type of functional group present which reacts the slowest. From the slope of the linear portion, which is equal to $[k(I - K_n)/2.303]$, the value of k (rate constant) for a particular step is calculated. This process is repeated by excluding the slowest reaction to get data for the next faster reaction, and so on, until a linear relation is obtained without any perceptible initial curved portion.

The time interval studied for all samples was between 5 min and 120 hr. Initial trials with a large number of oxycellulose samples showed that generally the titration readings remain more or less constant after periods longer than 120 hr. In few cases, however, where the reaction did not reach completion, the increase in acid content after 120 hr was quite insignificant. Slavik et al.² have also considered 120 hr as adequate for opening up most of the lactones in pulp samples. In order to determine the effect, if any, of liquor ratio on the estimated carboxyl content, measurements were carried out for 1 hr and 24 hr by taking different weights of phosphoric acid-sodium nitrite oxycellulose (0.25 to 1 g) as well as of D-glucuronic acid lactone (25 to 400 mg). Although the titration readings varied

naturally with the different weights taken, a constant value of carboxyl content was obtained irrespective of liquor ratio.

Study of Potassium Dichromate-Sulfuric Acid Oxycellulose (O_2)

The titration and acid content values for this oxycellulose for various periods between 5 min and 120 hr are given in Table I. The acid content values increase progressively and seem to reach a constant value after about 100 hr. From the plot of acid content values against period of contact, additional values of acid content were noted for other time intervals in order to obtain more data. These data were then used for the construction of subsequent graphs for rate analysis as shown in Figures 1 to 3. From these plots, the values of characteristic rates as well as

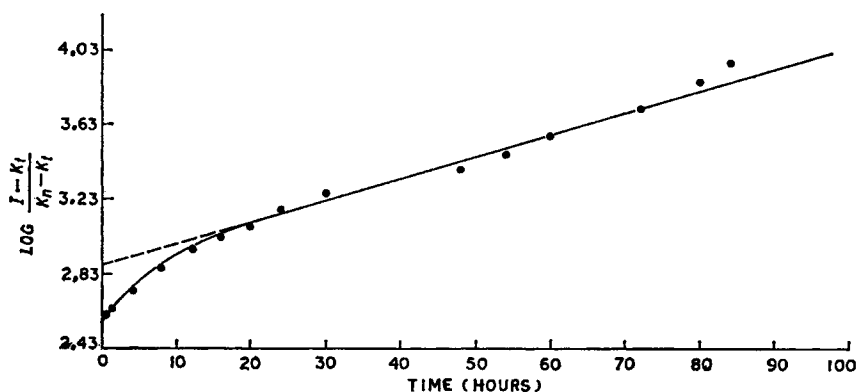


Fig. 1. Reaction rate curve for potassium dichromate-sulfuric acid oxycellulose (O_2).
First stage of calculation.

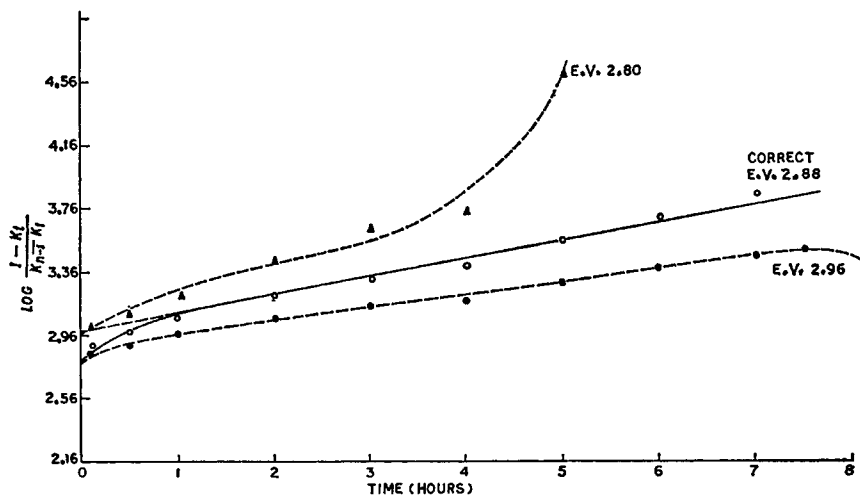


Fig. 2. Reaction rate curves for potassium dichromate-sulfuric acid oxycellulose (O_2).
Second stage of calculation.

TABLE I
Acid Content Values After Different Periods for Potassium
Dichromate-Sulfuric Acid Oxycellulose (O₂)

Time	Iodine reading, ml of 0.00888 <i>N</i>	Acid content, (meq acid/0.5 g) × 10 ²
5 min	0.975	0.85
30 min	1.075	0.94
1 hr	1.25	1.10
4 hr	1.60	1.41
8 hr	1.95	1.71
24 hr	2.55	2.24
48 hr	2.75	2.42
72 hr	2.90	2.55
96 hr	3.00	2.72
120 hr	3.00	2.72

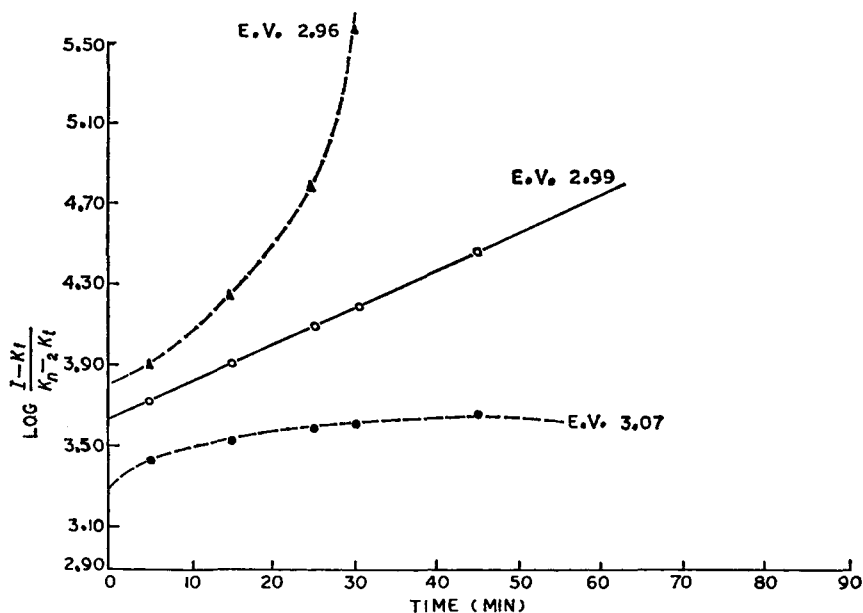


Fig. 3. Reaction rate curves for potassium dichromate-sulfuric acid oxycellulose (O₂).
Third stage of calculation.

amounts representing different types of acidic groups were obtained and are given in Table II. It can be noticed that there are three different types of acid groups with distinctly different rates and amounts. The first type represents the slowest-reacting acid groups, the second type reacts at a medium rate, while the third type of acid groups is found to have the highest reaction rate.

Extrapolation to zero time of the straight-line portion of the rate plot may seem uncertain. However, the method is self-checking. Even a

TABLE II
Characterization of Acid Groups in
Oxycelluloses Before and After Zinc Acetate Treatment

Sample	Oxidizing agent	Acid groups					
		First type		Second type		Third type	
		Rate k^a	Content ^b	Rate k	Content	Rate k	Content
S	standard cellulose	1.58	0.48	—	—	72.8	0.80
O ₂	K ₂ Cr ₂ O ₇ -H ₂ SO ₄	1.53	1.92	14.85	1.50	148.5	2.00
	O ₂ + Zn(OAC) ₂	1.32	1.44	16.47	1.86	—	—
O ₃	K ₂ Cr ₂ O ₇ -(COOH) ₂ . 2H ₂ O	1.03	5.41	18.00	1.56	790.0	0.53
	O ₃ + Zn(OAC) ₂	1.03	5.20	21.05	1.66	—	—
O ₆	HIO ₄	0.73	2.74	13.15	2.48	442.5	0.78
	O ₆ + Zn(OAC) ₂	1.10	2.74	26.27	2.26	—	—
O ₇	NaOCl	1.22	1.70	11.65	2.80	315.5	0.92
	O ₇ + Zn(OAC) ₂	1.10	1.42	14.90	3.20	—	—
O ₈	H ₃ PO ₄ -NaNO ₂	1.25	24.60	14.05	16.20	383.2	79.2
	O ₈ + Zn(OAC) ₂	1.03	22.00	9.08	42.00	200.4	25.6
O ₉	KMnO ₄	1.35	1.18	17.00	1.06	378.7	1.74
	O ₉ + Zn(OAC) ₂	1.40	0.92	18.00	1.28	—	—
O ₁₀	NaOBr	1.00	1.88	26.05	0.82	566.2	1.30
	O ₁₀ + Zn(OAC) ₂	0.95	1.68	35.50	0.82	—	—

^a Rate k in units of [(meq/l.)⁻¹ min⁻¹] × 10⁶.

^b Acid content in units of meq/100 g.

slight error on extrapolation makes the last portion of the next plot either rise steeply or fall gradually. During the first stage of rate analysis (Fig. 1), the accurate value of the extrapolation of the linear portion of the plot has been taken to be 2.88. But if the extrapolated values are taken a little above and below 2.88, say 2.80 and 2.96, the last portion of the curve in the next plot (Fig. 2) will show an abrupt steep rise or a gradual fall, respectively. Similarly, deviation from linearity can be clearly seen in the Figure 3 for the next stage, where the extrapolated values differ only slightly from the accepted value.

Results for Various Oxycelluloses

A summary of the results for the rest of the oxycelluloses is given in Table II. In general, three different types of acid groups with characteristic rates are obtained. In some of the oxycelluloses, such as phosphoric acid-sodium nitrite oxycellulose and potassium dichromate-oxalic acid oxycellulose, where reaction does not reach completion in 120 hr, there may be a possibility of a fourth type of extremely slow-reacting acid group.

All above oxycelluloses were subjected to a zinc acetate treatment and were analyzed for different types of acidic groups in a similar manner as described in detail above. The results are also given in Table II. From a study of the results for all oxycelluloses after zinc acetate treatment, it

TABLE III
 Characterization of Acid Groups in Oxycellulose
 After Sodium Borohydride Treatment

Sample	Acid groups					
	First type		Second type		Third type	
	Rate k^a	Content ^b	Rate k	Content	Rate k	Content
S	3.57	0.14	—	—	114.5	0.74
O ₂	2.60	1.70	—	—	135.75	2.05
O ₃	0.95	3.20	18.37	1.52	105.50	0.49
O ₆	0.82	1.22	—	—	157.8	0.58
O ₇	1.07	0.70	14.87	1.12	202.5	0.74
O ₈	1.18	15.12	—	—	107.5	77.0
O ₉	1.91	0.80	—	—	118.5	1.78
O ₁₀	1.37	1.24	—	—	150.0	1.36

^a Rate k in units of [(meq/l.)⁻¹min⁻¹] × 10⁶.

^b Acid contact in units of meq/100 g.

can be seen that a third type of fastest-reacting acid groups is absent. In samples such as phosphoric acid-sodium nitrite oxycellulose, whose content of the third type of acid group is initially very high, not all of these groups are blocked after zinc acetate treatment.

In the cases of the first and second type of acid groups, the rates for any sample are similar to the corresponding sample before zinc acetate treatment, and the amounts are roughly of similar order. The decrease in some cases may possibly be due to partial hydrolysis of the lactones occurring during zinc acetate treatment.³ In some cases, a little increase is noted in the second type of acid groups (especially in phosphoric acid-sodium nitrite oxycellulose) after the zinc acetate treatment. This is probably due to the partial lactonization of large amounts of free carboxyl groups present by the acetic acid evolved in the reaction medium.

Results for the oxycelluloses after sodium borohydride treatment are given in Table III. In most of the oxycelluloses, only two distinct rates are obtained, and the acidic groups of the second type having a medium rate of reaction are generally absent, while there is some reduction in the first type and no change in the third type. In the case of potassium dichromate-oxalic acid and sodium hypochlorite oxycelluloses, three rates are observed even after borohydride treatment, with decreased amounts of the first and second types of acidic groups (lactones). From the results, it seems that there is a preferential destruction of the second type of acid groups (lactones) in comparison to the first type (slowest-reacting lactones). Incomplete reduction of different types of lactones and preferential reduction of some types of lactones have been reported earlier.^{10,11}

The results of chlorous acid-treated oxycellulose samples are given in Table IV. Three types of acid groups with distinct rates are noticed in all the samples. The amounts of all acid groups show an increase after chlorous acid treatment of oxycellulose. The results of chlorous acid-

TABLE IV
 Characterization of Acid Groups in Chlorous Acid Modified
 Oxycelluloses Before and After Zinc Acetate Treatment

Sample	Acid groups					
	First type		Second type		Third type	
	Rate k^a	Content ^b	Rate k	Content	Rate k	Content
S	1.82	0.38	—	—	50.0	1.22
S + Zn(OAC) ₂	1.75	0.60	—	—	—	—
O ₂	1.42	4.40	15.20	2.80	445.0	7.40
O ₂ + Zn(OAC) ₂	1.50	3.50	18.40	3.50	—	—
O ₃	0.95	6.20	17.75	2.50	774.0	16.00
O ₃ + Zn(OAC) ₂	1.15	4.48	17.97	3.74	326.5	1.58
O ₆	0.90	4.52	22.17	4.20	690.0	25.00
O ₆ + Zn(OAC) ₂	1.16	4.10	19.30	5.00	—	—
O ₇	1.00	2.90	13.40	2.54	249.2	6.46
O ₇ + Zn(OAC) ₂	1.08	1.40	16.25	4.00	—	—
O ₈	1.13	22.0	13.35	20.20	224.3	93.00
O ₈ + Zn(OAC) ₂	1.19	31.0	12.78	44.00	206.9	30.00
O ₉	1.00	2.40	19.30	0.96	201.4	4.40
O ₉ + Zn(OAC) ₂	1.05	1.66	27.60	1.64	—	—
O ₁₀	1.05	2.90	26.62	0.96	183.0	3.40
O ₁₀ + Zn(OAC) ₂	0.95	2.20	26.30	1.68	—	—

^a Rate k in units of [(meq/l.)⁻¹min⁻¹] × 10⁶.

^b Acid content in units of meq/100 g.

modified samples after their zinc acetate treatment are also given in Table IV, showing generally an absence of the third type of acid groups. Potassium dichromate-oxalic acid and phosphoric acid-sodium nitrite oxycelluloses, having initially higher carboxyl contents, however show a very small value of the third type of acid groups, indicating that the zinc acetate treatment is not able to block all the carboxyl groups. For the first and second types of acid groups (lactones), the results follow a pattern similar to that of oxycelluloses and show values similar to those of corresponding chlorous acid-treated samples before zinc acetate treatment.

Reaction Rates of Some Model Compounds

Among the various model compounds used in the present study were sugar lactones of such types as are known to be present in oxycelluloses, viz., glucono- δ -lactone and glucuronic acid lactone. Other model compounds containing different functional groups, viz., free carboxyl and enediols, were also selected. The indirect iodometric titration method as well as the method of rate analysis used for model compounds were similar to those used for oxycelluloses. On the basis of rate analysis, the approximate ranges of various characteristic rates are given in Table V. The two types of lactones are found to react at different rates, which are however of a low order as compared to the reaction rates of free acids. It was found possible to characterize and approximately estimate the amounts of these two lactones by a rate analysis study in a 50:50 mixture. In the case of L-

TABLE V
Reaction Rates for Various Acidic Groups in Model Compounds

Reacting group (Model compound)	Range k^a
Glucuronic acid lactone	1-3.50
Glucono- δ -lactone	7-15
Free carboxyl (tartaric acid, oxalic acid and succinic acid)	170-185
Stable γ -lactone (ascorbic acid)	0.50-0.60
Enediol (ascorbic acid)	20-30

^a In units of [(meq/l.)⁻¹min⁻¹] $\times 10^6$.

TABLE VI
Range of Rates and pK Values for Various Acidic Groups in Oxycelluloses

Acid groups	Range k^a	Range of pK values	Groups responsible
First type	0.95-3.50	5.50-6.10	glucuronic acid lactone
Second type			
A	5-18	4.70-5.10	glucono- δ -lactone
B	17-35	4.40-4.75	C ₂ -C ₃ dicarboxyl lactone depending upon the nature of oxidation of cellulose
Third type	50-higher	3.00-4.30	free carboxyls

^a Rate k in units of [(meq/l.)⁻¹min⁻¹] $\times 10^6$.

ascorbic acid, the enediol groups seem to react at a faster rate, and complete reaction takes place in about 24 hr. The compound, however, continues to react further at a very slow rate and shows completion only after 300 hr, owing to a slow opening up of the stable γ -lactone. It was possible to analyze L-ascorbic acid and obtain two characteristic rates corresponding to enediol and stable γ -lactone, and the analyzed amounts were in fairly good agreement with the theoretically calculated values. The model compounds, however, react with KI-KIO₃ solution in a homogeneous medium. In contrast to this, the oxycellulose samples would react in a heterogeneous medium, and the actual rates observed are likely to be slightly lower, particularly in the case of slow-reacting lactone groups. Even in the heterogeneous medium, the relative rates of reaction of different acidic groups can be expected to agree with the relative rates under homogeneous medium. The approximate ranges of characteristic rate constants (k) of various acid groups observed in oxycelluloses are given in Table VI. From the range of rates thus observed for various types of acidic groups, the pK values ($-\log K$) were calculated for their characterization and are also given in Table VI.

DISCUSSION

General. A rate analysis study of the acid content after different periods of contact with KI-KIO₃ solution showed the presence of other types of acid

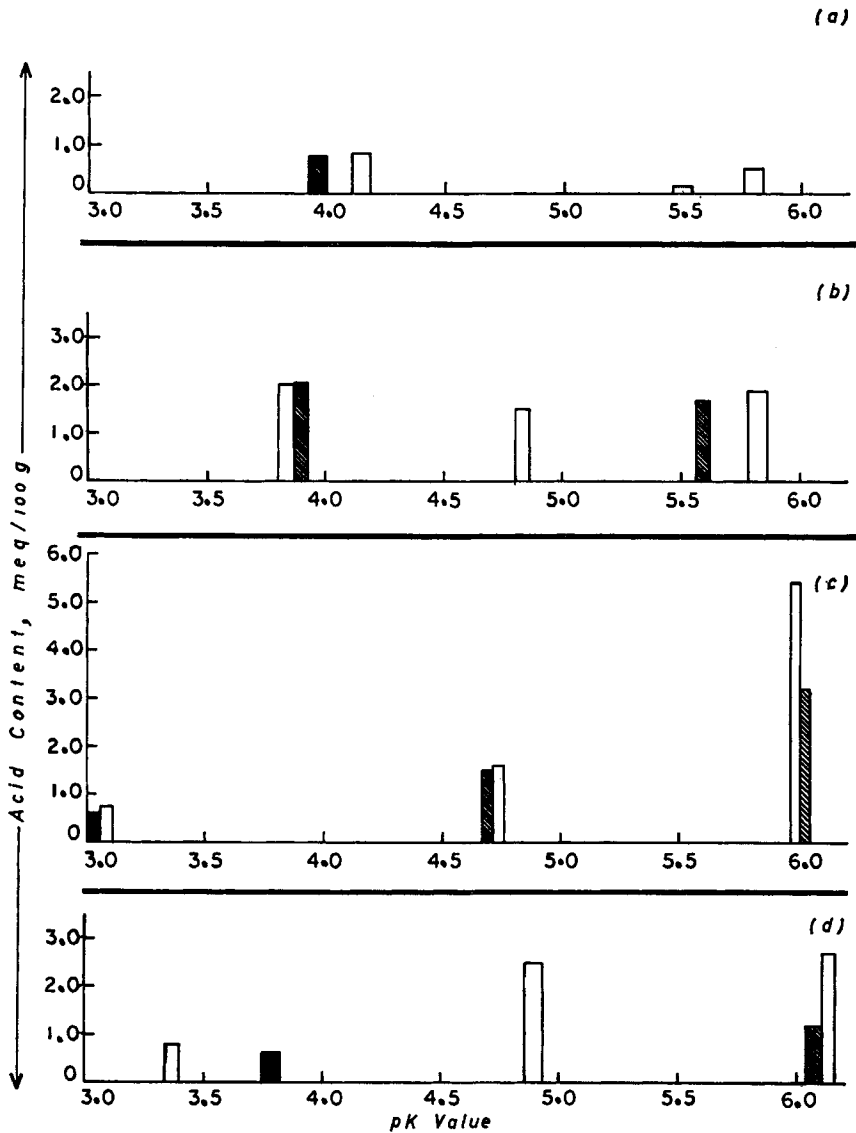


Fig. 4. Acidic group spectra: clear blocks, oxycellulose; lined blocks, oxycellulose after borohydride treatment; (a) standard cellulose (S); (b) O_2 ; (c) O_3 ; (d) O_6 .

groups besides free carboxyls in all the oxycelluloses and their modifications after sodium borohydride treatment. The data could be analyzed for each oxycellulose to obtain characteristic rates for different reacting species along with a rough quantitative analysis. An approximate characterization of acidic groups in any oxycellulose can thus be depicted graphically by plotting the content of a particular reacting group against its characteristic pK value, whereby a discontinuous diagram consisting of a number of peaks,

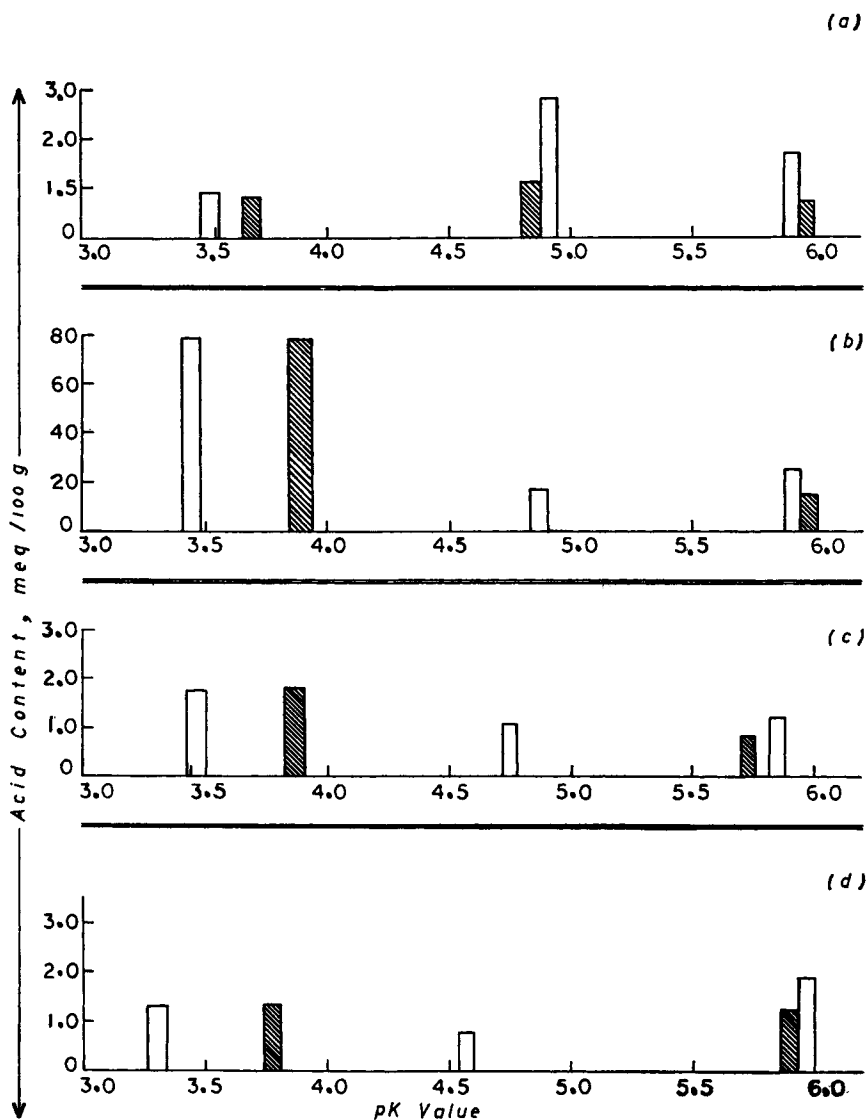


Fig. 5. Acidic group spectra: clear blocks, oxycellulose; lined blocks, oxycellulose after borohydride treatment; (a) O_7 ; (b) O_8 ; (c) O_9 ; (d) O_{10} .

each representing one particular type of acid group, is obtained. Such a representation of acidic groups can be designated as "acidic group spectrum" analogous to the carboxyl spectrum obtained by a similar rate analysis study of reaction with hydroxylamine hydrochloride by Sihtola and Neimo.⁸ Such acidic group spectra for different oxycelluloses as well as their borohydride-treated modifications are shown in Figures 4 and 5. For all the samples, the peak corresponding to free carboxyl groups ($pK \approx$

3-4) remains practically unaltered after sodium borohydride treatment, while the peaks for lactone are partially or completely destroyed.

Acidic Group Spectrum of Standard Cellulose (S). Two characteristic peaks (Fig. 4a) are obtained where the major portion of acidity can be attributed to free carboxyl groups ($pK \simeq 4.1$). Some acidity is also due to glucuronic acid lactone groups ($pK \simeq 5.8$). Weak positive tests for the presence of lactones as well as uronic acid groups were observed for standard cellulose.¹ After sodium borohydride treatment, the acidity due to glucuronic acid lactone decreases to a very low value.

Potassium Dichromate-Sulfuric Acid Oxycelluloses (O₂). Three characteristic peaks are obtained (Fig. 4b), one corresponding to free carboxyl ($pK \simeq 3.9$), the second corresponding to glucono- δ -lactone ($pK \simeq 4.8$), and the third corresponding to glucuronic acid lactone ($pK \simeq 5.9$). Some of the uronic acid groups formed on oxidation possibly lactonize during decationization, as observed by qualitative tests as well as increase in uronic acid content.¹ On sodium borohydride treatment, the glucono- δ -lactone peak disappears completely while some decrease is noticed for the glucuronic acid lactone peak.

Potassium Dichromate-Oxalic Acid Oxycellulose (O₃). Three peaks are obtained as in the case of O₂ (Fig. 4c); but relatively, the amount of lactone seems to be higher at the expense of free carboxyl groups. Appreciable decrease is noticed after borohydride treatment in the amount of glucuronic acid lactone ($pK \simeq 6.0$), while glucono- δ -lactone decreases to an insignificant extent. Acidic groups of the uronic type and lactones have been found mainly to be present in this oxycellulose in earlier work.^{1,13}

Periodate Oxycellulose (O₆). Although three peaks are seen in the spectrum of this oxycellulose (Fig. 4d), exact identification of specific lactones seems to be difficult). The second peak in the middle of the spectrum ($pK \simeq 4.9$) is quite appreciable and may be due to glucono- δ -lactone or C₂-C₃ dicarboxyl lactone (Table VI). The possibility of the presence of enediol groups seems less likely as they have a different pK value range and have not been detected by qualitative tests.¹ The third peak ($pK \simeq 6.1$) corresponds to some very slow-reacting unidentified lactone. The pK value is in the range for glucuronic acid lactone, but the presence of these groups in periodate oxycellulose has not been detected by qualitative tests or uronic acid estimation. After borohydride reduction, the second peak is absent, showing complete destruction of this lactone type, while the third peak ($pK \simeq 6.1$) is only partially destroyed.

Acidic Sodium Hypochlorite Oxycellulose (O₇). Three characteristics peaks are observed (Fig. 5a), one corresponding to free carboxyls ($pK \simeq 3.5$), the second due to glucono- δ -lactone ($pK \simeq 4.9$), and the third to glucuronic acid lactone ($pK \simeq 5.9$). On borohydride treatment, the amount of both lactones is decreased. The presence of lactone linkages and uronic acid groups has been qualitatively detected for this oxycellulose.¹ The presence of uronic acid groups in starch oxidized by hypochlorite has also been reported earlier.^{14,15}

Phosphoric Acid–Sodium Nitrite Oxycellulose (O₈). In the spectrum for this oxycellulose (Fig. 5b), three peaks each with high acid content are observed. The highest peak ($pK \simeq 3.7$) corresponds to free carboxyl groups, the second at $pK \simeq 5.0$ to glucono- δ -lactone, and the third ($pK \simeq 6$) to glucuronic acid lactone. After borohydride treatment, the second peak is absent, while the third peak is found to be appreciably decreased.

Alkaline Potassium Permanganate (O₉) and Sodium Hypobromite Oxycelluloses (O₁₀). The behavior of these two oxycelluloses is quite similar (Fig. 5c, d), and three peaks are observed in both. In addition to free carboxyl groups, the middle peak at pK 4.7 shows the presence of C₂–C₃ dicarboxyl, and the third peak ($pK \simeq 6$), of glucuronic acid lactone groups. On borohydride treatment, the second peak, corresponding to C₂–C₃ dicarboxyl lactone, disappears completely, while third decreases to some extent. The presence of C₂–C₃ dicarboxylic acids as well as uronic acid groups in alkaline pH-oxidized samples has been reported earlier.^{16–19}

Effect of Sodium Borohydride Treatment on lactones. The above results show that reduction of lactones by sodium borohydride takes place to different extents, and that even after 120 hr of treatment not all the lactone groups are completely destroyed. Lactones which are comparatively easily cleaved by the iodate–iodide solution are also easily reduced by sodium borohydride treatment, e.g., C₂–C₃ dicarboxyl lactone and glucono- δ -lactone. Preferential destruction of some lactone as compared to others by some reagents has been studied earlier.¹⁰ Hansoon et al.¹¹ have observed that reduction of lactones is influenced by the concentration of sodium borohydride and that glucono- δ -lactone is readily reduced as compared to arabino- γ -lactone.

CONCLUSIONS

Identification and rough quantitative estimation of various types of lactone groups has been shown to be possible in all oxycelluloses using the rate analysis study of reaction of acidic groups with KI–KIO₃ solutions. Most of the oxycelluloses show the presence of two types of lactone groups in addition to free carboxyl groups. Complete opening up of all lactone groups takes more than 120 hr; hence, the carboxyl content value by the iodometric method after 24 hr does not include all lactone groups. A rate analysis study of oxycelluloses after zinc acetate treatment gives information only about lactone groups as the free carboxyls are blocked. Sodium borohydride treatment destroys various lactones at different rates, and reduction is not complete even after 120 hr of treatment. Carboxyl content estimation after borohydride treatment of shorter periods would thus be affected by residual lactones present. An estimation of the total lactone content in oxycelluloses can also be obtained by the method of Norstedt and Samuelson^{20,21} involving pretreatment with alkaline salt solution. However, the method is unable to distinguish between various types of lactone groups. The rate analysis method using iodometric

estimation of acid groups suggested in the present work thus gives more information than is possible by other methods, as it characterizes as well as roughly estimates the lactone groups in oxycelluloses.

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