

# Characterization of Acidic Groups in Oxycelluloses

## III. Effect of Cation Freeing and Blocking on Estimation of Carboxyl Groups and Lactones by the Iodometric Method

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### Synopsis

A differentiation between free carboxyl and various lactone groups in different types of oxycelluloses was carried out based on the variation in their reaction rate with KI/KIO<sub>3</sub> solution. For oxycelluloses prepared under acidic conditions, a large proportion of carboxyl groups are present in free form. Each oxycellulose was also studied after cation freeing as well as after blocking the free carboxyl groups by treatment with sodium chloride.

Cation freeing was found to cause considerable lactonization of carboxyl groups; sodium chloride treatment blocked them only partially.

### INTRODUCTION

It has been shown by various workers that the acid treatment of cation freeing might give rise to lactonization, leading to a reduction in free carboxyl groups.<sup>1</sup> In earlier work a differentiation between carboxyl and lactones based on the variation in their reaction rate with KI/KIO<sub>3</sub> solution was carried out for oxycelluloses, as well as their modified products after sodium borohydride and chlorous acid treatments in the cation-free form.<sup>2</sup> These cation-freed samples were also subjected to a zinc acetate treatment and studied in a similar manner.<sup>2</sup> In the present work this aspect has been studied further by carrying out a rate analysis study of the iodometric reaction for oxycelluloses themselves, after cation freeing and after treatment with sodium chloride.

### EXPERIMENTAL

#### Preparation of Standard Cotton Cellulose

After 20's single yarn made from good quality Indian cotton was kier boiled and bleached under controlled conditions, the standard cotton cellulose was cut into 1-cm pieces for preparing the oxycelluloses.

#### *Preparation of Oxycelluloses*

Oxidation of standard cellulose with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> + (COOH)<sub>2</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> + H<sub>2</sub>SO<sub>4</sub>, and NaIO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> was carried out by treating 200 g of standard cellulose at 30°C M:L (1:50) (Table I).

For the preparation of N<sub>2</sub>O<sub>4</sub> oxycellulose, liquid N<sub>2</sub>O<sub>4</sub> was obtained by

TABLE I  
Conditions of Preparation of Oxycellulose

Designation	Oxidizing agent	Concentration	Time (h)
S	Standard cellulose	—	—
O <sub>1</sub>	Potassium dichromate + sulfuric acid	0.10 N 0.20 N	15
O <sub>2</sub>	Potassium dichromate + oxalic acid	0.20 N 1.00 N	4
O <sub>3</sub>	Sodium periodate + sulfuric acid	0.01 N 0.01 N	5
O <sub>4</sub>	Nitrogen dioxide/carbon tetrachloride	5.0 ml/L	6

condensing at  $-20^{\circ}\text{C}$  the gas evolved by the action of a mixture of one part of concentrated sulfuric acid and four parts of fuming nitric acid on sodium nitrite.<sup>3</sup> To 2 L of distilled anhydrous carbon tetrachloride was added 40 g of standard cellulose. The mixture was agitated, and 10 ml of liquid nitrogen dioxide was added from a graduated receiver. After the required time, the oxidized cellulose was filtered off, blown with hot air to remove volatiles, washed with  $\text{CCl}_4$ , and soaked in frequent changes of distilled water until the wash water was neutral to bromothymol blue indicator. The oxycelluloses were given repeated washing with distilled water, dried in air, and conditioned at 65% relative humidity (RH).

#### *Cation Freeing*

Cation freeing was carried out by treating 20 g of oxycellulose with 0.5 M hydrochloric acid (M:L, 1:50) for  $\frac{1}{2}$  h followed by washing with carbon dioxide-free distilled water, air drying, and conditioning at 65% RH.

#### *Treatment of Sample with Sodium Chloride*

A total of 20 g of each oxycellulose was treated with a 1% solution of sodium chloride for 2 h. It was then washed with distilled water until the wash water gave no precipitate with silver nitrate solution. The oxycellulose was then air dried and conditioned at 65% RH.

#### *Determination of Acid Content of Oxycellulose*

The acid content was determined by the indirect iodometric titration method.<sup>4</sup>

#### *Determination of Copper Number*

Copper number was determined by Heyes method and expressed as the amount of copper reduced from the cupric to the cuprous state by 100 g of cellulose material.<sup>5</sup>

### **Results and Discussion**

Four oxycelluloses with different contents of functional groups were prepared using dichromate with sulfuric acid as well as oxalic acid, periodate with sulfuric acid, and nitrogen-dioxide. Each oxycellulose was studied in

three different states, designated as  $O_n$ , oxycellulose;  $O_n$  (CF), oxycellulose after cation freeing; and  $O_n$  (NaCl), oxycellulose after NaCl treatment.

The details of the differential kinetic rate analysis method to differentiate between free carboxyl and lactone groups in oxycelluloses have been discussed in the earlier work.<sup>2</sup> An approximate characterization of acid groups in oxycelluloses can be depicted graphically by plotting the amount of a particular reacting group against its characteristic pK value ( $-\log k$ ). Oxycelluloses in general contained three types of acid groups, first or slow-reacting (pK value, 5.5–6.1), second type or medium reacting (pK value, 4.4–5.1), and third type or fast-reacting free carboxyl (pK value, 3.00–4.3). The results of kinetic rate analysis are given in Table II, and Figure 1 shows the acidic group spectrum of oxycellulose  $O_1$ ,  $O_2$ , and  $O_4$ .

#### Potassium Dichromate-Sulfuric Acid Oxycellulose ( $O_1$ )

The oxycelluloses  $O_1$ ,  $O_1$  (NaCl), and  $O_1$  (CF) have three types of acidic groups to different extents. For all three oxycelluloses, the calculated value of  $\log(I/K_{n-2})$  corresponds to the value of  $I_3$ , which is the intercept on  $Y$  axis of the third-stage plot of  $\log[(I - K_t)/(K_{n-2} - K_t)]$  versus time. This suggests that there are no extremely fast reacting groups present, which is another self-checking test of the kinetic analysis.

From Figure 1A it is seen that the oxycellulose itself has a large amount of free carboxyl groups. On sodium chloride treatment both the free carboxyl and slow-reacting groups are decreased, but this treatment, unlike zinc acetate treatment, does not block all the free carboxyl groups.<sup>2</sup> On cation freeing the free carboxyl groups are decreased and the medium and slow-reacting groups are not much affected.

#### Potassium Dichromate-Oxalic Acid Oxycellulose ( $O_2$ )

This oxycellulose shows only the presence of two types of acid groups, medium and fast; the slow type is absent. However, the intercept of a second-stage plot of  $\log[(I - K_t)/(K_{n-1} - K_t)]$  is not equal to  $\log(I/K_{n-1})$ ; hence there may be extremely fast reacting groups present and their amount was obtained from the equation

$$I_2 = \log \frac{I - K_{n-2}}{K_{n-1} - K_{n-2}}$$

where  $K_{n-2}$  is the amount of these extremely fast reacting groups. Their rate cannot be measured accurately since the carboxyl content measurements involve a time period below 5 min. Hence, they have been included along with the third type in the spectrum and are indicated by an asterisk in Table II. In  $O_2$  (NaCl) three types of acid groups are present, and the  $Y$  intercept of the third-stage plot  $I_3$  is equal to  $\log(I/K_{n-2})$ , clearly indicating that there are no extremely fast reacting groups. However, the amount of free carboxyl is reduced considerably by this treatment, with the appearance of the I type of slow-reacting groups. The cation-freed samples have three types of acid groups, and in addition the extremely fast reacting are similar to  $O_2$ ; hence for this oxycellulose, slow-reacting lactones are formed on cation freeing.

TABLE II  
 Characterization of Acidic Groups in Oxycelluloses Before and After Cation Freeing and NaCl Treatment

Sample	Oxidizing agent	First type		Second type		Third type	
		Rate $k^a$	Content <sup>b</sup>	Rate $k$	Content	Rate $k$	Content
S	Standard cellulose	1.15	0.94	25.0	0.38	139.0	0.43
O <sub>1</sub>	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> /H <sub>2</sub> SO <sub>4</sub>	1.55	2.40	12.0	1.66	87.21	2.80
O <sub>1</sub> (NaCl)		1.40	1.25	20.0	1.55	428.0	1.58
O <sub>1</sub> (CF)		1.20	2.65	16.50	1.50	508.0	1.40
O <sub>2</sub>	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> /(COOH) <sub>2</sub> · 2H <sub>2</sub> O	Absent	Absent	6.5	2.56	256.0	1.32 + 1.5*
O <sub>2</sub> (NaCl)		0.82	0.60	11.0	1.44	146.0	1.1 + 0.0
O <sub>2</sub> (CF)		1.60	1.28	26.0	0.52	126.0	1.1 + 2.48*
O <sub>3</sub>	NaIO <sub>4</sub> /H <sub>2</sub> SO <sub>4</sub>	1.0	5.8	Absent	Absent	90.0	1.0
O <sub>3</sub> (NaCl)		0.50	5.62	17.0	0.90	190.0	0.54
O <sub>3</sub> (CF)		0.50	2.60	23.0	0.92	152.0	1.3
O <sub>4</sub>	N <sub>2</sub> O <sub>4</sub> /CCl <sub>4</sub>	0.50	2.13	9.5	1.60	146.0	2.8 + 6.9*
O <sub>4</sub> (NaCl)		4.40	1.88	Absent	Absent	340.0	3.36 + 0.0
O <sub>4</sub> (CF)		0.85	4.00	31.0	1.33	154.0	1.0 + 8.0*

<sup>a</sup> Rate  $k$  in units of  $[(\text{mEq/L})^{-1} \text{min}^{-1}] \times 10^6$ .

<sup>b</sup> Acid content in units of mEq per 100 g.

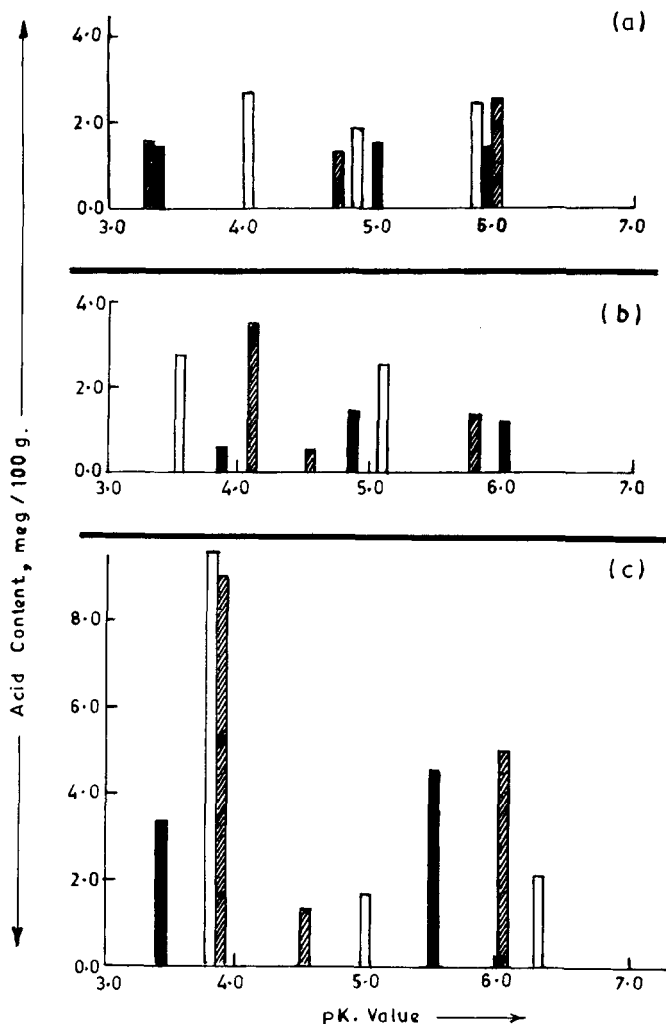


Fig. 1. Acidic group spectra. Clear: oxycellulose; solid: oxycellulose after NaCl treatment; hatched: oxycellulose after cation freeing. (a), O<sub>1</sub>; (b) O<sub>2</sub>; (c) O<sub>4</sub>.

### Periodate-Sulfuric Acid Oxycellulose (O<sub>3</sub>)

Periodate oxidation is very specific and gives rise to aldehyde groups at the 2,3-position of the glucose unit in cellulose. Hence, we expect that the nature and type of acidic groups should be similar to those of standard cellulose. However, all of them show an increased amount of all three types of acidic groups, especially the slow type. During the carboxyl estimation there was no leveling off of carboxyl content, even after 120 h; on the contrary it increases rapidly after 30 h. The kinetic calculations are based on the theory of simultaneous reaction occurring at decreasing rates. Another primary assumption of the differential rate analysis study is that all reactions are completed in 120 h for oxycelluloses.<sup>2</sup> In periodate oxycellulose there are significant side reactions taking place after about 30 h, which results in the high value for the first type of acid group.

Periodate oxycelluloses, after carboxyl content determination at various time periods, were washed with excess distilled water and dried and the copper number determined. There is a continuous fall in copper number with the length of the iodometric reaction, showing that reducing groups may be interfering in the iodometric reaction. No significant change in copper number is observed for other oxycelluloses, namely, O<sub>2</sub> (Table III). Hence the differential kinetic rate analysis is unsuitable to measure accurately carboxyl and lactones in periodate oxycelluloses.

#### Nitrogen Dioxide Oxycellulose (O<sub>4</sub>)

Nitrogen dioxide oxycellulose is known to contain a large amount of carboxyl at the C<sub>6</sub> position. From the acidic group spectrum (Figure 1C), we see that the non-cation-free oxycellulose has all three types of acid groups, along with very fast reacting carboxyl. After sodium chloride treatment the second type of lactone is lost and also the very fast reacting carboxyl is completely blocked. The intercept of the second-stage plot  $I_2$  is equal to  $\log(I/K_{n-1})$ , indicating there are no more faster reacting groups present.

On cation freeing the amount of fast-reacting free carboxyl remains the same but large amount of the *I* type of lactones are formed, which are the glucuronic acid lactones.

### CONCLUSIONS

Both the dichromate-oxalic acid and nitrogen-dioxide oxycelluloses contain some very fast carboxyls, which could be the C<sub>6</sub> primary carboxyl, and NaCl treatment completely blocks these groups.

Cation freeing gives rise to lactonization; an acid wash might also lead to dissolution of highly oxidized material. Hence, for oxycelluloses prepared under acidic conditions, cation freeing could be omitted before the carboxyl estimation by the iodometric method. The intercept of the last-stage plot is a good guideline to check the rate analysis method and also to determine the presence of any fastest reacting groups.

Periodate oxycelluloses cannot be analyzed for acidic groups by the iodometric method due to interfering oxidation reactions after a period of contact of more than 24 h.

TABLE III  
Copper Number After Different Periods of Carboxyl Estimation

Time (h)	Copper number of oxycellulose	
	O <sub>3</sub>	O <sub>2</sub>
0	8.45	6.3
3	7.8	6.4
10	7.5	6.3
30	5.8	6.5
70	5.0	6.6
120	4.1	6.6

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