

STUDIES IN OXYCELLULOSE

Part III. Oxidation of Cellulose with a Mixture of Nitrogen Dioxide and Oxygen

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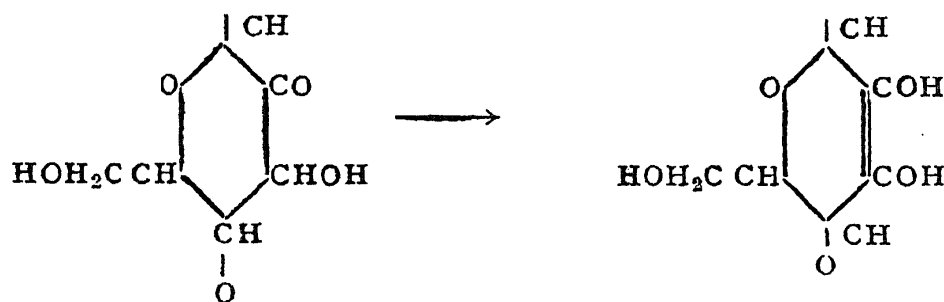
INTRODUCTION

KENYON and co-workers¹⁻⁴ have studied the oxidation of cellulose with nitrogen dioxide at room temperature (21° C.), and their conclusions may be summarised as follows:

(i) Nitrogen dioxide oxidises cellulose to give highly acidic products—designated celluronic acids—which dissolve in dilute alkali when the carboxyl content is 13.5% or more as determined by the carbon dioxide evolution method.

(ii) Nitrogen dioxide preferentially converts the primary alcoholic groups to carboxyl and is said to leave the glucosidic linkages unaffected.

In one of their communications they have described an investigation of the oxidation of cellulose by nitrogen dioxide dissolved in carbon tetrachloride and have suggested a mechanism of oxidation of cellulose.³ In their latest contribution⁴ to this subject, Kenyon and co-workers have examined the alkali lability of celluronic acids and have concluded that to a certain extent a secondary alcoholic group is oxidised to a keto group which in presence of alkali gives rise to an ene-diol thus:



Evidence in favour of Kenyon's conclusions has been supplied by Head⁵ and by Rowen, Hunt and Plyer.⁶

Examination of the literature reveals that no work has been carried out on the oxidation of cellulose by a mixture of nitrogen dioxide and oxygen

except for a paper,⁷ which is available to the authors only in the form of an abstract. In this abstract it has been stated that the oxidation of cellulose by oxygen is catalysed by nitrogen dioxide. The present investigation has been undertaken with a view to elucidate the mechanism of oxidation of cellulose by a mixture of nitrogen dioxide and oxygen, since it is felt that this would be distinctly different from the one postulated by Kenyon and collaborators referred to above.

A number of oxycelluloses have been prepared using nitrogen dioxide alone and in admixture with oxygen as oxidants. A few samples of periodic acid and dichromate oxalic acid oxycelluloses were also prepared. Their properties such as copper number, carboxyl content, cuprammonium fluidity, effect of alkali treatment on copper number, etc., have been studied before and after treatment of the oxycelluloses with chlorous acid.

GENERAL DETAILS OF EXPERIMENTAL METHODS

Materials

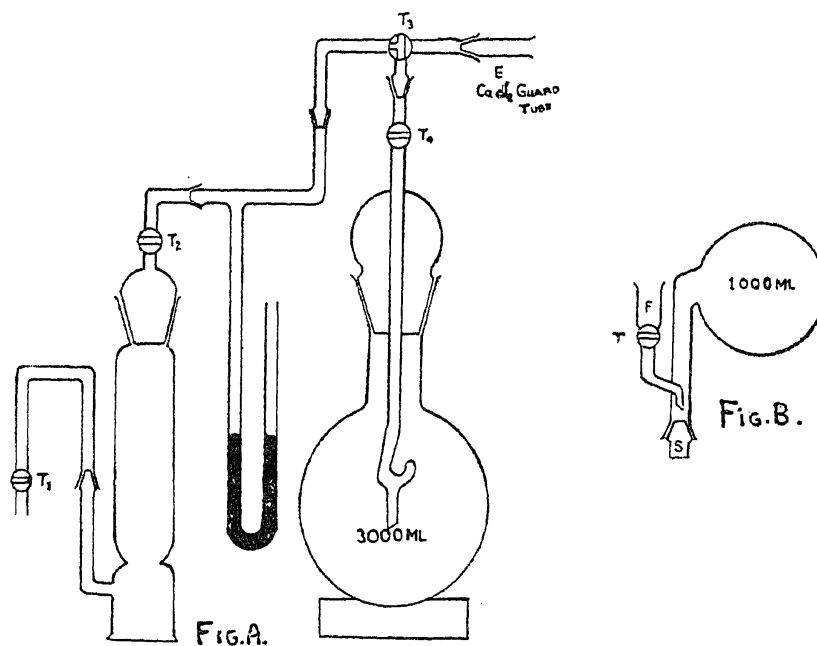
Cotton.—The material used for oxidation is carefully purified and bleached 18's yarn made from Indian cotton. In the preliminary experiment the material has been oxidised in the form of hanks. Later, for convenience of manipulation, oxidations have been carried out with the above yarn cut into 1" lengths. In all experiments the cotton cellulose is dried at 105-10° C. for 2 hours and cooled in a desiccator.

Liquid nitrogen dioxide.—The gases evolved by the action of a mixture of one part conc. sulphuric acid and four parts of fuming nitric acid on anhydrous sodium nitrite are dried by passage over fused calcium nitrate and phosphorous pentoxide and condensed in a receiver cooled in a freezing mixture. The gases condense to a deep green liquid which is oxidised by bubbling dry oxygen. The oxidation is considered to be complete when the liquid no longer possesses any greenish tint. The liquid which is bright orange in colour, is stored in oxygen atmosphere under slight pressure for at least 48 hours. Prior to use the liquid is distilled over phosphorous pentoxide and condensed in a receiver cooled by immersion in crushed ice. During the preparation, storage and distillation the nitrogen dioxide is protected against atmospheric moisture by means of calcium chloride guard tubes.

The nitrogen dioxide prepared as described is used in (a) gaseous form, (b) in solution in freshly distilled dry carbon tetrachloride and (c) in admixture with oxygen for oxidation of cellulose.

Details of apparatus used for oxidation.—For oxidation of cotton cellulose with a mixture of nitrogen dioxide and oxygen, the arrangement of

apparatus used is shown diagrammatically in Fig. A. Where pure nitrogen dioxide has been used as the oxidant either in gaseous state or as a solution in carbon tetrachloride, the flask shown in Fig. B, is used. In the preliminary experiments the reaction vessel was a 10 l. bottle with a ground-in-stopper carrying a glass hook for suspending the hank. The apparatus is enclosed in an air thermostat maintained at 35° C.



Arrangement of Apparatus used for Oxidation of Cellulose

The following methods of oxidation have been used:

Method A: Oxidation of cellulose by a mixture of nitrogen dioxide and oxygen under pressure.—The various parts of the apparatus are dried in a current of hot air and assembled as shown in Fig. A. Cotton yarn in the form of a hank is suspended from the hook. The drying tower contains fused calcium nitrate as the desiccant.

The assembled apparatus is evacuated through T₁ till the manometer registers a vacuum of 25" of mercury. Then T₁, T₂, T₃ and T₄ are closed and the T piece containing the three-way tap T₃ is disconnected. A measured volume of freshly distilled liquid nitrogen dioxide is introduced into the upper tube of T₄ and the liquid is sucked in by opening T₄. As soon as the whole of the liquid is sucked in T₄ is closed and the apparatus is again restored to its original assembled position. T₂, T₃ and T₄ are opened, T₁ is connected to an oxygen cylinder and oxygen introduced by opening T₁. When the requisite pressure is attained, T₁, T₂, T₃ and T₄ are closed. The reaction is allowed to proceed for a predetermined time. At the end of the

reaction period the drying tower is disconnected and the residual gases removed by evacuation. The oxycellulose is transferred to a large beaker containing cold distilled water and washed with repeated changes till free from acid. The material is dried carefully at room temperature away from light and dust, conditioned and carefully stored.

Method B: Oxidation of cotton cellulose with a mixture of nitrogen dioxide and oxygen at atmospheric pressure.—In this case a mixture of nitrogen dioxide and oxygen has been prepared as described above, but the addition of oxygen is stopped as soon as the mixture attains atmospheric pressure. The mixture is allowed to stand overnight after closing T_2 and T_4 . The dried material is then introduced by momentarily removing the ground-in-stopper of the reaction vessel. The stopper is immediately placed in position. At the end of the reaction period the residual gases are removed and the oxycellulose is washed, dried and stored as described earlier.

Method C: Oxidation of cotton cellulose with pure nitrogen dioxide.—The apparatus shown in Fig. B is used. The flask containing the weighed amount of cotton cellulose is heated at $105-10^{\circ}$ C. for two hours and immediately stoppered to prevent contact with moisture. The flask is then evacuated as completely as possible through T using a Hyvac pump. T is then closed, the Hyvac pump is disconnected and a measured volume of freshly distilled anhydrous liquid nitrogen dioxide is poured from a measuring cylinder into the funnel F. The liquid is sucked in by opening T, which is closed as soon as all the liquid has gone in. The liquid falls into the hollow stopper S from which it rapidly evaporates to fill the flask with nitrogen dioxide fumes. The flask is kept in an air-thermostat maintained at 35° C. for the requisite period. At the end of this period, the gases are removed by evacuation and the oxycellulose is washed free from acid, dried and stored as before.

When a solution of nitrogen dioxide in carbon tetrachloride is used as the oxidant the method is modified as follows. A weighed amount of cotton—dried as mentioned earlier—is suspended in a known volume of anhydrous redistilled carbon tetrachloride in the flask shown in Fig. B. It is evacuated till the carbon tetrachloride starts boiling vigorously at 35° C. T is then closed and the pump disconnected. A known amount of freshly distilled dry liquid nitrogen dioxide is introduced as before which collects in the hollow stopper S. The liquid is then dissolved by rapidly inverting and shaking the flask a number of times, so that a homogeneous solution of nitrogen dioxide in carbon tetrachloride is obtained. At the end of the reaction period the oxidised sample is separated from the solution by filtration, washed free from acid, dried and stored as mentioned earlier.

Periodic acid and dichromate-oxalic acid oxycelluloses.—These have been prepared and rendered cation-free as described in an earlier communication.⁸

Treatment of the oxycelluloses with chlorous acid.—The various oxycelluloses are treated with 0.1 M sodium chlorite in 0.5 M phosphoric acid for 18 hours at room temperature.⁹ The samples are then washed, rendered cation free, air-dried and carefully stored.

Determination of combined nitrogen.—The nitrogen content of the sample has been estimated by De-varda's method.¹⁰

Determination of copper number.—Due to the high copper number of the oxycellulose samples, a modification of Heyes' method^{11, 8} has been used. As in many cases, the sample is completely disintegrated during the copper number determination, the precipitate of cuprous oxide is filtered through a G₄ sintered glass crucible instead of the usual G₂ grade.

Determination of copper number after alkali treatment.—It has been observed during the examination of the alkali solubility of the oxycelluloses produced by method A that their solution in dilute caustic soda (0.25 N) does not give any precipitate on acidification if the solution is kept aside for sufficient time prior to acidification. The same change is effected by heating the alkaline solution on a boiling water-bath for fifteen minutes. Hence it is evident that hydrolysis takes place both during storage and by heating. With a view to examine the effect of alkali treatment on the reducing power of the oxycelluloses the following method has been used.

The sample (0.1 g.) is weighed and transferred to a Pyrex test tube (6" × $\frac{3}{4}$ "). Caustic soda solution (10 ml. of 0.25 N) is poured over the sample and the sample distributed throughout the solution by means of a thin glass rod. The test tube is heated by immersion in a boiling water-bath for 15 minutes. The mouth of the test tube is closed by means of a pear-shaped glass bulb. At the end of 15 minutes the test tube is cooled in running water and the contents transferred to a 100 ml. Pyrex conical flask. The test tube is rinsed out into the conical flask with 9 ml. of distilled water divided into three lots. The caustic soda is then neutralised by addition of 1 ml. of 2.5 N sulphuric acid. Glucose solution (10 ml. of 0.04% solution) is added to the mixture followed by addition of a boiling mixture of sodium carbonate-bicarbonate solution (75 ml.), copper sulphate solution (5 ml.) and sodium carbonate -bicarbonate mixture (3 : 1; 4 g.). The rest of the procedure is as for the usual copper number determination. A blank determination is also carried out without any cotton.

*Determination of carboxylic acid content.*¹²—The carboxylic acid content of the oxycelluloses has been determined by Neale and Stringfellow's Alkali titration method, with suitable modification. The cation-free sample [0.5 g. (0.25 g. if $-\text{COOH} > 9\%$)] is suspended in a mixture of 25 ml. of 5% sodium chloride, 25 ml. of N/50 caustic soda (carbonate-free) and 25 ml. of carbon dioxide-free distilled water. At the end of one hour the excess of caustic soda is backtitrated with 0.02 N hydrochloric acid using 0.04% bromocresol purple solution as indicator.

Neale and Stringfellow's method for the determination of the carboxyl content has been criticised strongly by Kenyon,¹³ and by Davidson.^{9, 14} The latter has shown that it gives fictitious values for highly reducing oxycelluloses. The carboxylic acid content in the above oxycelluloses has also been determined by the Iodometric method developed in this laboratory.⁸ This method does not involve the use of alkali. In this method 0.5 g. (0.25 g. if $-\text{COOH}$ is more than 9%) of the cation-free sample is suspended in a mixture of 25 ml. of $\text{KIO}_3 : \text{KI} : \text{NaCl}$ solution (21.4 g. : 83 g. : 50 g. respectively per litre) and 25 ml. of carbon dioxide-free distilled water. After standing for twenty-four hours the mixture is titrated against 0.02 N iodine using starch solution as indicator. The carboxyl content is expressed as milliequivalents of carboxyl per 100 g. of the dry material.

Determination of cuprammonium fluidity.—The cuprammonium hydroxide solution used in the determinations has been prepared according to the method described by Pacsu and Mehta,¹⁵ and the fluidity determinations have been carried out by the method recommended by the B.C.I.R.A.¹⁶

Due to the highly degraded nature of the oxycelluloses a 1% solution has been used for the determination.

EXPERIMENTAL RESULTS AND DISCUSSION

The chemical properties and behaviour of the nitrogen dioxide + oxygen oxycelluloses prepared as described earlier are summarised in Tables I and II and represented graphically in Figs. 1, 2, 3 and 4.

In Table I are given the results of oxycelluloses obtained by using the oxidant under pressure. From Figs. 1 and 2 it is evident that while carboxyl content by Neale's method increases progressively with the time of oxidation, the copper number increases very rapidly and attains a maximum value at an early stage of oxidation and then remains constant. If the oxycelluloses are treated with alkali prior to copper number determination it is found that the copper number falls to nearly a third of its original value. Oxycelluloses thus obtained are progressively more soluble in dilute caustic soda solu-

TABLE I

Oxidation of cellulose with a mixture of nitrogen dioxide and oxygen

Time of reaction hours	Carboxyl content (Neale's method) in milliequivalents per 100 g. of material	Copper number			Solubility in alkali				Nitrogen content %
		Before treatment with alkali	After treatment with alkali	COOH content per cent.	2% caustic soda		1% caustic soda		
					After 5 minutes	Overnight contact	After 5 minutes	Overnight contact	
4	76.6	59.51	25.02	3.45Insoluble....	Insoluble....		1.35
8	123.5	71.01	26.37	5.5650 per cent. soluble....				..
16	160.3	87.25	25.36	7.2075 per cent. soluble.....				1.94
24	177.3	86.56	25.36	7.9895 per cent. soluble.....				2.37
40	202.8	86.56	25.02	9.13completely soluble.....				1.81

Material: 20 g. of bone-dry cotton in 10 l. flask.

Oxidant: 10 ml. of nitrogen dioxide (measured at 0° C.) + oxygen till the pressure of the mixture is 15" of mercury above the atmospheric pressure.

TABLE II

Oxidation of cellulose with a mixture of nitrogen dioxide and oxygen at atmospheric pressure

Time of reaction hours	Carboxyl content (Neale's method) in milliequivalents per 100 g. material	Copper number	
		Before treatment with alkali	After treatment with alkali
8	49.91	71.68	
16	66.62	76.76	29.08
24	71.91	77.09	
32	79.25	78.45	28.53
40	96.99	74.39	
48	99.63	84.52	25.69

tion (1% or 2%) and become more or less completely soluble after the $-\text{COOH}$ content has reached 8% or more. Maximum solubility appears to have been attained after five minutes contact with alkali and longer periods upto about 24 hours seem to have no appreciable effect. Shrinkage is first observed when the $-\text{COOH}$ content is about 5% and then increases progressively with an increase in $-\text{COOH}$ content, reaching a maximum shrinkage of about 75% of the original length when the carboxyl content is about 9%. The oxycellulose samples which are soluble in dilute caustic soda solutions are also soluble in dilute solutions of sodium carbonate, quaternary ammonium hydroxides and in warm aqueous pyridine. Though they retain their fibrous structure

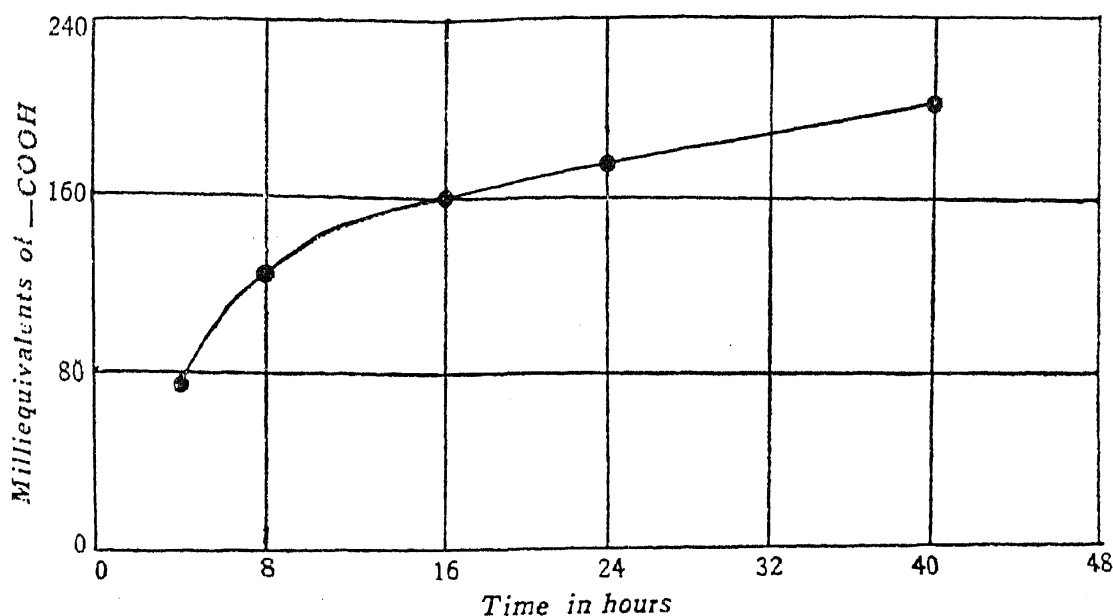


FIG. 1

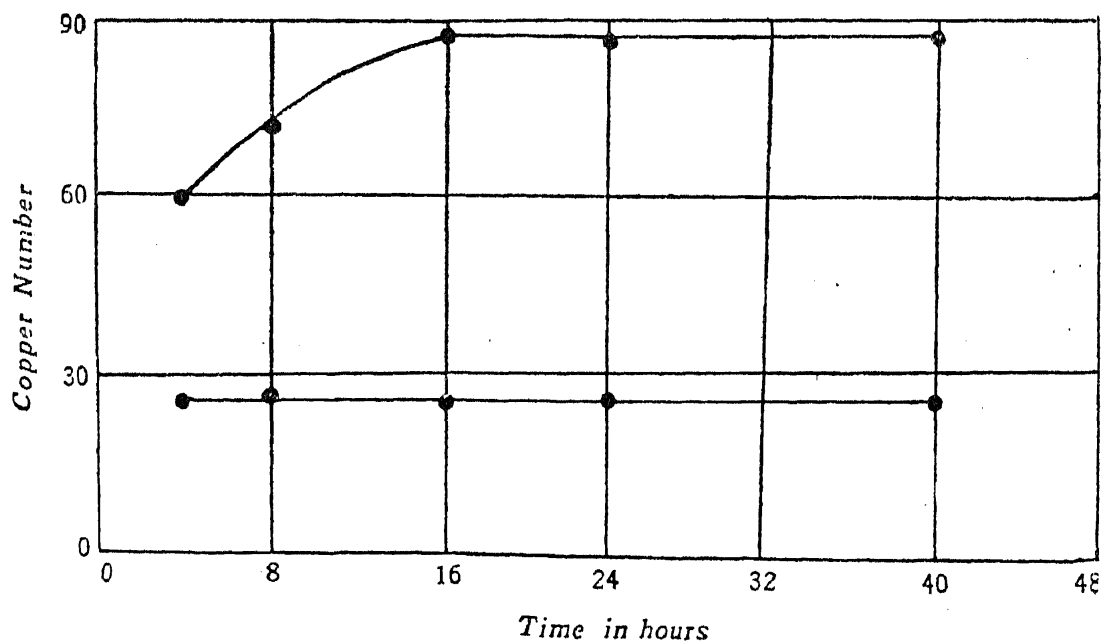


FIG. 2

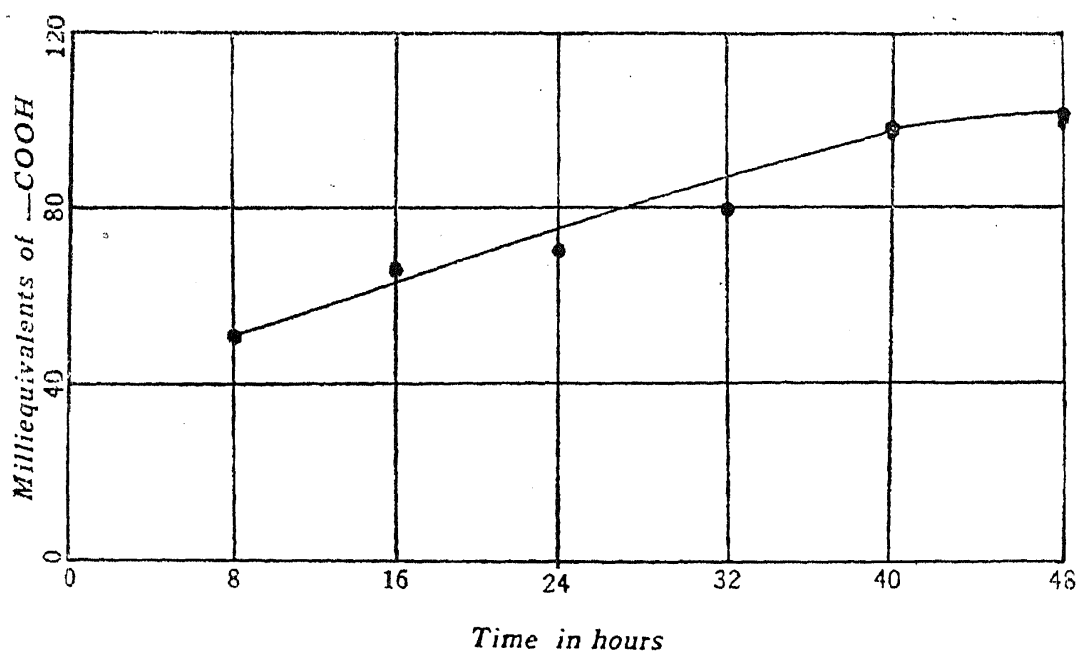


FIG. 3

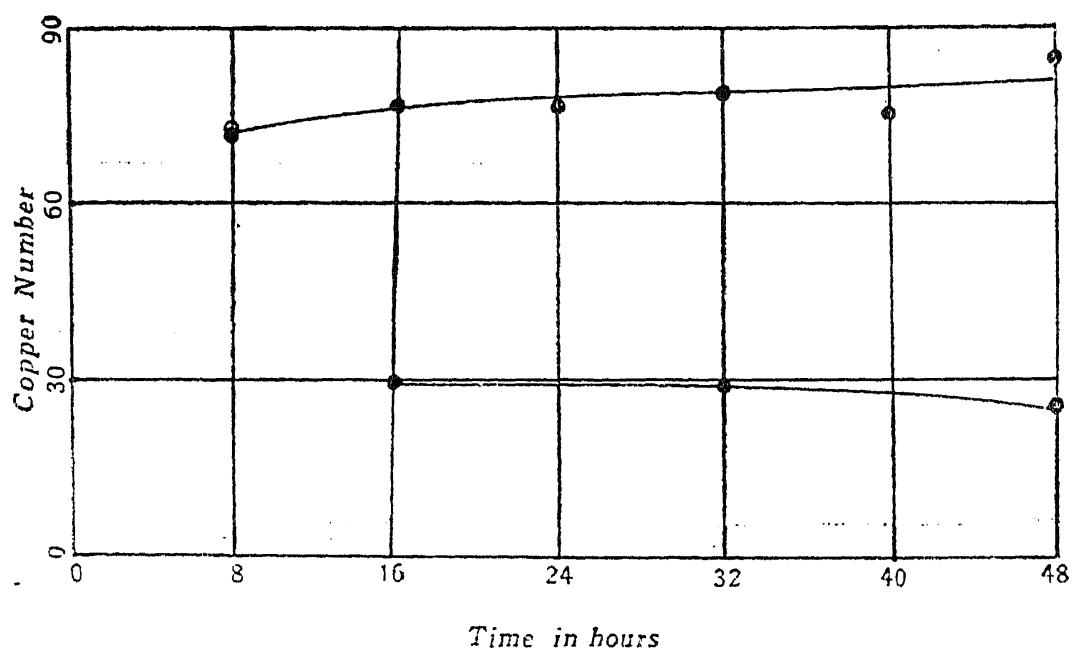


FIG. 4

Materials : 20 g. bone-dry cotton in 101. flask. Oxidant : 10 ml. of nitrogen dioxide (measured at 0° C.) + oxygen till the pressure of the mixture is atmospheric.

even with a high degree of oxidation, their fluidities in cuprammonium hydroxide are very high. Thus a 2% solution of an oxycellulose possessing a -COOH content of 9% is 76 reciprocal poises, while the fluidity of the solvent at the same temperature (30° C.) is 99.2 reciprocal poises.

In Table II are summarised the properties of oxycelluloses obtained using a mixture of nitrogen dioxide and oxygen at atmospheric pressure. The relation between the time of oxidation and carboxyl content and copper number are represented graphically in Figs. 3 and 4 respectively. It is evident

that though the carboxyl content by Neale's method increases progressively with the time of oxidation, the copper number is more or less constant and is reduced to about $\frac{1}{3}$ on treatment with alkali. No shrinkage is observed even after 48 hours and the oxycelluloses obtained are not at all soluble in dilute alkali. However, these products exhibit behaviour similar to the products obtained with the oxidant under pressure, with reference to (a) rise in copper number with time of reaction and (b) fall in copper number on treatment with alkali (compare Tables I and II and Figs. 2 and 4).

From Tables I and II it is seen that the amount of nitrogen dioxide in the gaseous mixture is the same, only the percentage of oxygen is different. An examination of the above tables and Figs. 1, 2, 3 and 4 brings out clearly the influence of the proportion of oxygen in the oxidation mixture, *viz.*,

(a) The rate of reaction is nearly doubled with a higher proportion of oxygen.

(b) The reaction seems to have come more or less to a standstill with the reaction mixture containing a lower proportion of oxygen while with the higher proportion of oxygen the rate of reaction seems to be appreciable even after 48 hours. Further the curve for the rate of reaction in the latter case resembles that obtained by Kenyon¹⁷ for oxidation of cellulose with nitrogen dioxide (*cf.* Fig. 5).

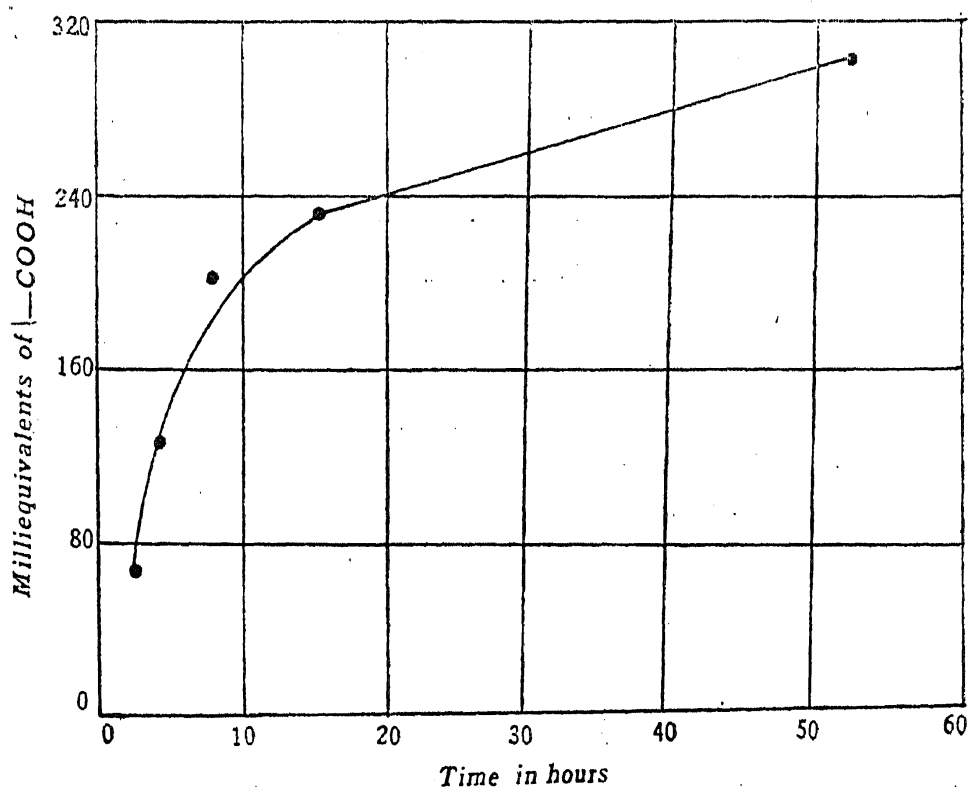


FIG. 5

(c) In presence of oxygen, the copper number increases rapidly to a maximum and then remains constant. Alkali treatment results in a fall to approximately one-third of the original.

A comparison of the properties of the nitrogen dioxide + oxygen oxycelluloses (Method A, *cf.* Table I) with nitrogen dioxide oxycelluloses studied by Kenyon and collaborators, is summarised in Table III. Under Kenyon's oxycellulose the original observations of Kenyon, *et al.*, have been summarised.

TABLE III

Kenyon's nitrogen dioxide oxycellulose	Nitrogen dioxide + oxygen oxycellulose
(i) Alkali-soluble only when carboxyl content is 13.5% or more. Samples with lower carboxyl content only swell in dilute alkali	(i) Completely soluble in alkali when carboxyl content is about 9%, but is partly soluble when carboxyl content is above 3.5%
(ii) Shrinkage and surface hardening observed when the carboxyl content is more than 15%	(ii) Shrinkage and surface hardening observed with a carboxyl content of 5.5% and above
(iii) Oxidation comes more or less to a standstill when the carboxyl content has attained a value of 25% (the theoretical value for poly-anhydro-glucuronic acid)	(iii) Attempts to prepare pure samples with more than 13.5% carboxyl did not succeed due to excessive swelling of the product in water to form a gel during washing treatment
(iv) Copper number increases progressively with oxidation. The copper number increases on treatment with alkali. This observation is not recorded by Kenyon and others, but has been observed in the present investigation (<i>cf.</i> Table V)	(iv) Copper number rises rapidly, reaches a maximum value at an early stage of oxidation and then remains constant. On treatment with alkali copper number falls to one-third of the original
(v) Highly oxidised products are hydrolysed by boiling water and the aqueous extract darkens on further boiling	(v) Highly oxidised samples are only partly hydrolysed by boiling water. The aqueous extract does not darken on boiling

SIMILARITIES

- (1) Both products are highly acidic, possess great affinity for basic dyes and metal ions, and retain their fibrous structure even though highly oxidised.
- (2) In aqueous solution sodium salts are precipitated on addition of a water-miscible non-solvent, *e.g.*, ethyl alcohol.
- (3) Polyvalent cations form insoluble salts.

From the foregoing, it is evident that nitrogen dioxide + oxygen oxycelluloses (hereafter designated as Oxycellulose I) possess distinctly different properties from the nitrogen dioxide oxycelluloses of Kenyon (hereafter designated as Oxycellulose II.)

Comparison of the chemical properties of oxycellulose I, oxycellulose II, periodic acid oxycellulose and dichromate-oxalic acid oxycellulose.—Due to

the excessive handling necessary for the preparation and complete analysis of the oxycellulose samples it was felt that a considerable portion will be lost thus rendering the final sample far from truly representative of the original oxycellulose. Further, it has already been shown that from the point of view of chemical behaviour there is no difference between the two oxycelluloses described in Tables I and II respectively. Therefore moderately oxidised samples of oxycellulose I have been prepared by Method B. Side by side samples of oxycellulose II and two specific oxycelluloses, *viz.*, periodic acid and dichromate-oxalic acid oxycelluloses of a moderate degree of modification have been prepared for comparison. They have been examined with respect to carboxyl content (Neale's method¹² and Iodimetric method⁸) copper number, effect of alkali treatment on copper number and nitrogen content before and after treatment with chlorous acid (Table V).

Due to the high reducing power exhibited by some of the samples, a few samples have been treated with chlorous acid for 18, 42 and 66 hours respectively. The solution of chlorous acid is replaced by a fresh lot of the solution after the first eighteen hours. From the results summarised in Table IV it is evident that treatment with chlorous acid for eighteen hours is sufficient. Hence all the samples described in Table V have been treated with chlorous acid for eighteen hours only.

TABLE IV

Effect of time of treatment with chlorous acid

Properties	Oxycellulose I No. 1	Time of treatment with chlorous acid in hours			Oxycellulose II No. 7	Time of treatment with chlorous acid in hours		
		18	42	66		18	42	66
Carboxyl content in milliequivalents per 100 g. of the material—								
Alkalimetry ..	58.5	65.4	65.0	65.4	82.4	88.1	88.4	88.1
Iodimetry ..	57.2	63.5	63.5	63.5	84.3	90.6	89.6	90.1
Copper number ..	37.7	34.6		34.6	17.0	15.3		15.3
Combined nitrogen %	0.72	0.72		0.72	0.13	0.13		0.13

TABLE V

Comparison of the chemical properties of nitrogen dioxide + oxygen, nitrogen dioxide, periodic acid and dichromate — oxalic acid oxycelluloses

Sam- ple No.	Type of oxycellulose and method of preparation	Carboxyl content in milli- equivalents per 100 g. of material				Copper number				Increase in carboxyl content (4) - (2) = (9)	Fall in copper number before alkali treatment (5) - (7) = (10)	Copper number equivalent (9) : (10) = (11)	Colour of alkaline extract during pre- treatment with alkali chlorous acid		Combined nitrogen content %		Fall in copper number due to alkali treatment	
		Before treat- ment with chlorous acid		After treat- ment with chlorous acid		Before treat- ment with chlorous acid		After treat- ment with chlorous acid					Before treat- ment with chlorous acid	After treat- ment with chlorous acid	Before treat- ment with chlorous acid	After treat- ment with chlorous acid		
		Iodi- metry (1)	Iodi- metry (2)	Nalcs (3)	Iodi- metry (4)	Before alkali treat- ment (5)	After alkali treat- ment (6)	Before alkali treat- ment (7)	After alkali treat- ment (8)									
1	<i>Oxycellulose I</i> Method B (3 ml. NO ₂ + 10 g. cotton) Time of reaction 2 hrs. " " 4 hrs. (4 ml. NO ₂ + 10 g. cotton) Time of reaction 2 hrs. " " 4 hrs.	58.5	57.2	65.4	63.5	37.7	15.45	34.6	15.6	6.3	3.1	2.06	D. Y.	Y.	0.72	-22.2	-19.0	
2		72.5	72.8	76.5	78.0	40.6	19.1	38.0	18.1	5.2	2.6	2.0	D. Y.	Y.	0.90	-21.5	-19.9	
3		22.6	20.6	33.48	29.30	14.2	9.18	10.2	7.94	8.7	4.0	2.18	D. Y.	Y.	0.40	-5.02	-2.26	
4		63.0	59.1	67.9	69.0	37.1	16.3	32.3	14.6	9.9	4.8	2.06	D. Y.	Y.	0.80	-20.8	-17.7	
5	<i>Oxycellulose II</i> (up to 10) (Gaseous NO ₂ oxidant) 3.5 ml. NO ₂ for 10 g. cotton in 3 l. flask 2 hrs. " " 4 hrs. 3.5 ml. NO ₂ for 10 g. cotton in 1 l. flask 2 hrs. " " 4 hrs. (Oxidant: Nitrogen di- oxide dissolved in CCl ₄) 10 g. dry cotton treated with 4 ml. NO ₂ (0° C.) in 175 ml. of dry CCl ₄ for 4 hours	11.1	10.1	13.1	13.2	6.02	6.5	2.58	3.1	3.1	3.44	0.90	L. Y.	P. C.	0.14	+ 0.48	+ 0.52	
6		33.1	31.6	35.1	36.2	9.75	10.2	4.73	5.1	4.6	5.02	0.92	L. Y.	P. C.	0.16	+ 0.45	+ 0.37	
7		82.4	84.3	88.2	90.1	17.0	..	11.7	..	5.8	5.3	1.09	L. Y.	P. C.	0.13	- ..	- ..	
8		119.9	121.4	119.9	124.3	20.1	21.2	17.12	19.3	2.9	3.0	0.97	L. Y.	P. C.	0.16	+ 1.1	+ 2.18	
9			32.59	36.14	37.81	6.43	6.93	3.01	3.77	3.42	3.42	1.00	L. Y.	P. C.	0.16	+ 0.50	+ 0.76	

10	30 g. dry cotton treated with 5.1 ml. NO_2 (0°C.) in 500 ml. dry CCl_4 for 4 hours	16.1	16.8	20.3	20.5	8.74	11.64	4.49	5.65	3.7	4.25	0.87	L. Y.	P. C.	0.0	+ 2.9	+ 1.16
11	Product 10 oxidised with 0.01 M HIO_4 for 48 hours at room temperature	49.6	16.8	69.6	72.0	26.8	19.4	5.46	6.88	55.2	21.34	2.59	Y.	P. C.	0.0	- 7.4	+ 1.42
12	<i>Oxycellulose III</i> 21.2 g. (air-dry) cotton treated with 0.01M HIO_4 for 48 hours	30.1	2.29	47.6	46.8	19.0	12.3	1.53	1.53	44.5	17.47	2.54	Y.	P. C.	..	- 6.7	+ 0.0
13	21.2 g. (air-dry) cotton treated with 0.005 M HIO_4 for 48 hours	12.7	2.66	25.2	25.3	10.2	8.1	1.02	1.05	22.6	9.18	2.46	Y.	P. C.	..	- 2.1	+ 0.03
14	<i>Oxycellulose IV</i> 21.2 g. (air dry) cotton treated with 0.4N $\text{K}_2\text{Cr}_2\text{O}_7$ in N oxalic acid for 4 hours	8.58	7.87	24.4	25.6	20.2	21.3	2.54	3.2	17.73	17.66	1.00	Y.	P. C.	..	+ 1.1	+ 0.66
15	21.2 g. (air-dry) cotton treated with 0.2N $\text{K}_2\text{Cr}_2\text{O}_7$ in N oxalic acid for 4 hours	5.50	4.92	16.0	15.3	11.73	12.5	1.53	2.55	10.38	10.2	1.02	Y.	P. C.	..	+ 0.77	+ 1.02

D. Y. = Deep Yellow; Y. = Yellow; L. Y. = Light Yellow; P. C. = Practically colourless.

In the above table only the mean of two independent determinations are given for the sake of convenience of expression.

Maximum variation from mean value ± 0.2 units for carboxyl content.

" " " " " ± 0.1 unit for copper number.

A few samples have been examined for cuprammonium fluidity before and after treatment with chlorous acid. The results are summarised in Table VI.

TABLE VI

Effect of treatment with chlorous acid on cuprammonium fluidity

Material	Cuprammonium Fluidity 1% solution				Decrease in cuprammoni- um fluidity %
	1	2	3	Mean	
<i>Oxycellulose I</i>					
No. 1	52.6	50.9	49.8	51.1	
Above treated with chlorous acid	31.8	..	31.2	31.5	38.4
No. 2	50.7	51.1	49.4	50.4	32.4
Above treated with chlorous acid	33.7	..	34.5	34.1	
<i>Oxycellulose II</i>					
No. 5	28.9	..	29.0	28.95	
Above treated with chlorous acid	23.9	23.7	23.8	23.8	17.7
No. 6	41.5	40.8	41.1	41.1	
Above treated with chlorous acid	34.2	34.5	35.7	34.8	15.3
<i>Oxycellulose III</i>					
No. 12	53.0	51.5	53.1	52.5	
Above treated with chlorous acid	29.6	29.9	..	29.8	43.1
<i>Oxycellulose IV</i>					
No. 14	31.6	..	31.0	31.3	
Above treated with chlorous acid	25.4	26.0	25.6	25.7	18.0

The similarities and dissimilarities between the four oxycelluloses are summarised below:

1. For the same degree of oxidation, as measured by carboxyl content, I possesses a higher copper number as compared with II.

2. I possesses a higher percentage of combined nitrogen than II.

3. On treatment with chlorous acid the carboxyl content as determined by the Iodimetric method increases and copper number decreases in both the cases. But if the value of the "copper number equivalent" (*cf.* Table V) is examined it is found that for II and IV the value is nearly unity, for III and

nitrogen dioxide periodic acid oxycellulose No. 11, (which has a preponderance of dialdehyde groups) the value is near about 2.5, while for oxycellulose I it is between 2 and 2.2 which is much nearer to 2.5 than to unity. Another noteworthy point is the small amount of free aldehyde present, (as shown by treatment with chlorous acid) in comparison with the carboxyl groups in the oxycelluloses.

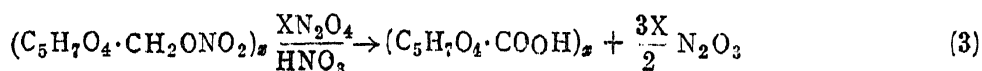
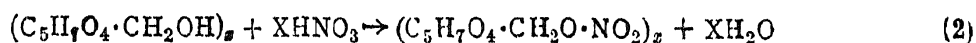
4. I suffers a fall in copper number on treatment with alkali, both before and after treatment with chlorous acid, while II and IV show an increase in copper number under similar treatment. On the other hand however, III suffers a fall in copper number prior to treatment with chlorous acid, but alkali treatment has practically no effect on copper number, if the sample has been pretreated with chlorous acid. The anomalous behaviour of oxycellulose No. 11 is interesting in that, prior to treatment with chlorous acid, alkali treatment results in a fall in copper number, while pretreatment with chlorous acid reverses the effect of alkali treatment.

5. All the oxycelluloses suffer a fall in cuprammonium fluidity on treatment with chlorous acid. A careful examination of Table VI reveals that the percentage decrease is of the same order for oxycelluloses I and III, and II and IV respectively.

6. Further, it may be observed that during treatment with alkali in the course of the study of the effect of alkali treatment on copper number, oxycelluloses II, III, IV and No. 11 give yellow coloured extracts with alkali, if they have not been pretreated with chlorous acid. On pretreatment with chlorous acid however, the alkaline extracts obtained are practically colourless. With oxycellulose I, however, pretreatment with chlorous acid results in a decrease in the colour intensity of the alkaline extract, still the colour of the alkaline extract is quite appreciable.

Mechanism of oxidation.—In the foregoing pages the difference between oxycelluloses I and II have been clearly brought out. Kenyon, *et al.*, have shown that when cellulose is oxidised by nitrogen dioxide the primary alcoholic group is oxidised to carboxyl.^{1,2} After an investigation³ into the oxidation of cellulose by solutions of nitrogen dioxide in carbon tetrachloride they have suggested a mechanism of oxidation. According to these authors, the oxidation of cellulose involves at least two steps, the first of which is nitration. They maintain that it is virtually impossible to prepare an anhydrous cellulose, as powerful desiccants ultimately begin to remove the "water of constitution" from cellulose. Hence they conclude that some nitric acid will be present in any scheme for oxidising cellulose with nitrogen dioxide. The nitration is more or less limited to the primary hydroxyl group in presence

of nitrogen dioxide. The second step is denitration-carboxylation by nitrogen dioxide which is catalysed by the nitric acid present. Thus the mechanism of oxidation of cellulose by nitrogen dioxide may be represented by the following:



Now it is evident from the above equations that the concentration of nitrogen dioxide decreases progressively with time. However, if oxygen is present the dinitrogen trioxide (N_2O_3) formed is immediately reoxidised to nitrogen dioxide. Thus the effective concentration of nitrogen dioxide will be maintained more or less constant as long as any oxygen is present. In this manner a much higher rate of oxidation of the cellulose by nitrogen dioxide may be expected in presence of excess of oxygen. Another interesting possibility is the side by side oxidation of cotton cellulose during the reoxidation of dinitrogen trioxide to nitrogen dioxide. Auto-oxidations of this type are well known both in organic and inorganic chemistry.¹⁸⁻²⁴

In the foregoing pages it has been shown that when cellulose is oxidised with a mixture of nitrogen dioxide and oxygen, the products obtained differ from Kenyon's oxycelluloses. Thus it is evident that in addition to the oxidation of the primary alcoholic group in 6-position to carboxyl, some other position is also being oxidised in the cellulose molecule when a mixture of nitrogen dioxide and oxygen is used as the oxidant. From the earlier analysis of the experimental results it can be concluded that nitrogen dioxide + oxygen oxycelluloses possess the following groups:

(a) Carboxyl groups as indicated by the Iodimetric method.

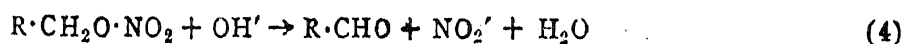
(b) Free aldehyde groups as shown by increase in carboxyl content and decrease in copper number on treatment with chlorous acid.

(c) A substantial proportion of the aldehyde groups are of the type that are present in periodic acid oxycelluloses, as seen from the "copper number equivalent" of 2 to 2.2 shown by these oxycelluloses as compared with 2.5 the corresponding value for periodic acid oxycelluloses (*cf.* Table V). This is further borne out by the degree of decrease in cuprammonium fluidity exhibited by these oxycelluloses on treatment with chlorous acid (*cf.* Table VI).

(d) A group which exhibits reducing properties on treatment with alkaline Braid solution, but not affected by chlorous acid, but which is substantially destroyed by treatment with strong alkali. This is probably

the nitrate group present in these oxycelluloses and which accounts for the combined nitrogen. A glance at Table V will show that these oxycelluloses possess a higher percentage of combined nitrogen than nitrogen dioxide oxycelluloses.

In attempting to explain the mechanism of decomposition of nitric acid esters by alkalis Berthelot²⁵ suggested that it may take place in the following way:

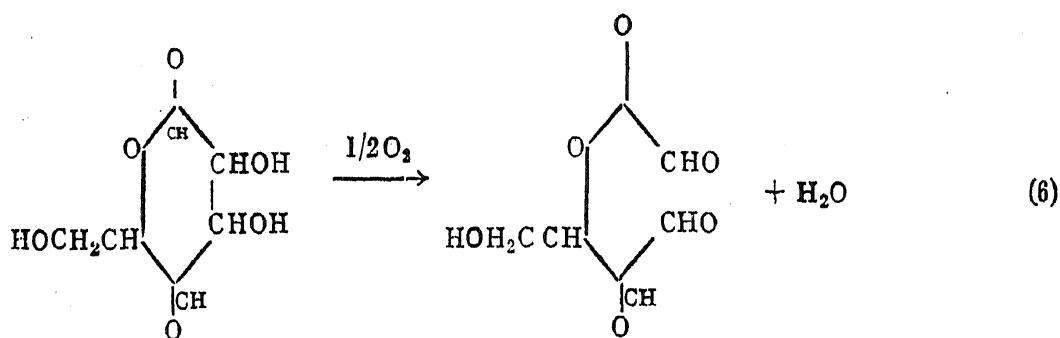
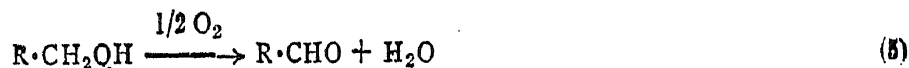


Further Kenyon and Grey²⁶ have shown that cellulose nitrates decompose intramolecularly with the reduction of nitrate nitrogen to nitrite, and oxidation of the cellulose molecule to simple organic acids. It is also well known that during the saponification of cellulose nitrate with alkali, the decomposition products formed exert a reducing effect on the sodium nitrate, so that the latter is partially converted into nitrite and partly into nitrogen and ammonia.²⁷⁻²⁹

If it is assumed that equation (4) represents the reaction that takes place in presence of the weak alkali of the Braidy solution, then the high copper number of these oxycelluloses can be explained. Further, if in presence of the stronger alkali employed in the pre-treatment, it is assumed that the reactions suggested by Kenyon and Gray,²⁶ and other workers,²⁷⁻²⁹ take place, then the substantial fall in copper number exhibited by these oxycelluloses on treatment with strong alkali can also be accounted for. This is further substantiated by the fact that the oxycellulose No. 11, which contains the dialdehyde type of grouping, suffers a fall in copper number on alkali treatment. But if the same oxycellulose is first treated with chlorous acid, alkali treatment has exactly the opposite effect on copper number, as the dialdehyde groups have been rendered insensitive by treatment with chlorous acid.

Thus it appears that during the oxidation of cellulose with a mixture of nitrogen dioxide and oxygen a certain amount of nitration takes place. Also at the same time the ring structure appears to be ruptured at the 2 : 3 position with the formation of a dialdehyde as in the periodic acid oxidation of cellulose in addition to the carboxyl. The exact position of the carboxyl group is very difficult to fix as it may be formed in the 6-position as suggested by Kenyon's mechanism or by partial oxidation of the dialdehyde with nitrogen dioxide to the corresponding dicarboxylic acid. The small proportion of the free aldehyde in comparison with the carboxyl content in these oxycelluloses as also in nitrogen dioxide oxycelluloses can be explained if it is assumed that the first stage in the oxidation is the

formation of the aldehyde either in the 6-position or the dialdehyde in the 2 : 3 position, thus:



The second stage will be the oxidation of these aldehyde groups to carboxyl groups by the nitrogen dioxide present. Now if the oxidation of $-\text{CHO} \rightarrow \text{COOH}$ is much more rapid than the formation of $-\text{CHO}$ as described above then the small amount of free aldehyde can be easily accounted for.

SUMMARY

(i) When cellulose is oxidised with a mixture of nitrogen dioxide and oxygen the products obtained (I) dissolve in dilute alkali when the carboxyl content is about 9% as compared with a minimum of 13.5% required for alkali solubility in case of nitrogen dioxide oxycelluloses (II).

(ii) I usually possesses a higher percentage of combined nitrogen than II.

(iii) The yellow colour developed on treatment with hot dilute caustic soda disappears more or less completely if the oxycelluloses (except I) are treated with chlorous acid. In case of I, the intensity of the colour is diminished considerably.

(iv) There is a greater decrease in cuprammonium fluidity on treatment with chlorous acid with I and periodic acid oxycelluloses as compared with II and dichromate oxalic acid oxycelluloses.

(v) On treatment with alkali there is a fall in copper number both in the case of I and periodic acid oxycellulose while an increase in copper number takes place in the case of II and dichromate-oxalic acid oxycellulose. Based on the above conclusions a tentative mechanism of oxidation has been suggested for the oxidation of cellulose with a mixture of nitrogen dioxide and oxygen.

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