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Investigation of the Properties of Cellulose Oxidized by Nitrogen Dioxide. V. Study of Mechanism of Oxidation in Presence of Carbon Tetrachloride[1]

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The early investigations of the oxidation of cellulose by nitrogen peroxide recognized the apparent specificity of the point of attack in the anhydro-β-D-glucose unit and the absence of extensive nitration of the final celluronic acid.[1a] Vapor phase reaction in a closed system which retains nitric oxide and nitrogen trioxide, or in an open system in which at least part of these gases escape, produces celluronic acids of similar properties. The amount of carboxyl generated in the cellulose depends on the ratio of nitrogen peroxide to cellulose[3] and the contact time.[3] The chemical behavior of the celluronic acids indicates that the C_6 or primary hydroxyl is converted to a uronic acid carboxyl.[2,3]

Subsequently, it was shown[4] that cellulose may be oxidized with solutions of nitrogen dioxide in an inert diluent, such as carbon tetrachloride. Celluronic acids so made appear chemically indistinguishable from those of similar carboxyl contents prepared by vapor phase oxidation.

Throughout this work it was noted that there is a very small amount of combined nitrogen in the final product. Heretofore no attempt has been made to ascertain the mechanism involved in the oxidation. This paper describes an investigation of some pertinent points concerning the mechanism of the oxidation of cellulose using solutions of nitrogen peroxide in carbon tetrachloride.

Experimental

Materials.—Cellulose surgical gauze of 20/12 count obtained from Parke, Davis and Company was used in all experiments. This gauze had been subjected to a mild bleach by hydrogen peroxide. The cellulose was of high viscosity, about 900 poises, in cuprammonium hydroxide solution. In some oxidations gauze was used as such, while in others it was comminuted in a Wiley mill to pass a 20-mesh sieve. The physical form employed is indicated for each series of experiments. In every case the cellulose was dried at 110° for two hours just prior to use.

Carbon tetrachloride of commercial grade was purified by washing in a solution of aqueous 50% sodium hydroxide and ethanol, separating the layers, washing with distilled water repeatedly, drying over calcium chloride, filtering, and distilling through a glass helix-packed column, and retaining the fraction boiling between 76.0 and 76.5°.

Nitrogen Tetroxide (N_2O_4).—The starting material used in the rectification was crude nitrogen peroxide (NO_2–N_2O_4) obtained from the nitric acid recovery plant of the Eastman Kodak Company. It was distilled at atmospheric pressure, in apparatus shown diagrammatically in Fig. 1. Reflux ratio was maintained at 6:1. The considerable forerun generally obtained froze to a bluish color in the receiver, indicating the presence of small amounts of nitrogen trioxide, and was discarded. When a colorless liquid, freezing to a clear, transparent solid in the receiver, began to accumulate, a 50-cc. sample was collected and the freezing point accurately determined by means of a cooling curve. The clear glass-like solid was collected until it began to show a very faint yellow color, indicating the presence of nitric acid. The colored material and the remainder of the material in the still were discarded.

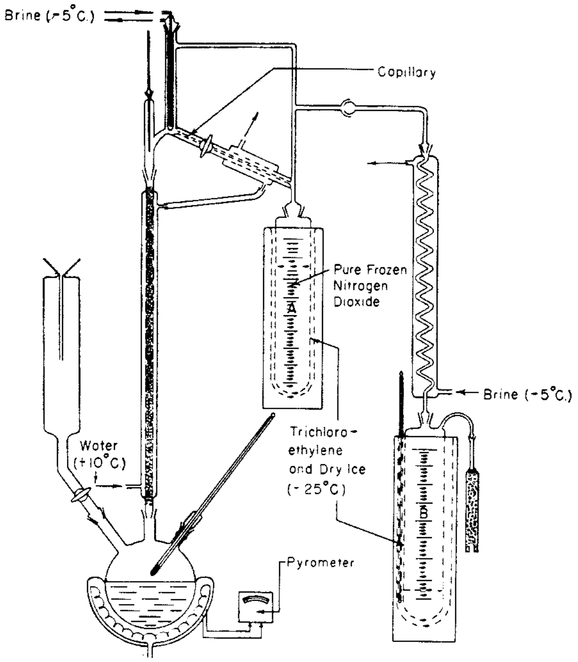

Fig. 1.—Distillation apparatus for nitrogen dioxide.

The apparatus designed specifically for the freezing point determinations, shown in Fig. 2, was operated as follows: With the nitrogen tetroxide reservoir (A) empty and the stopcock (B) open, anhydrous nitrogen was run through the apparatus for ten minutes prior to use. The nitrogen supply was removed by breaking the flow between the cylinder and the drying bottles, thus maintaining anhydrous conditions in the nitrogen-filled chamber. The stopcock (B) was promptly closed and the reservoir immediately filled with the nitrogen tetroxide sample. The stopcock (B) was opened and 60 cc. of nitrogen tetroxide was admitted promptly into the freezing chamber. This amount is much less than the total amount of nitrogen tetroxide present in the reservoir, A; thus any hydrolysis or reaction with atmospheric oxygen must take place at the top—at the atmosphere-liquid interface. Therefore, the portion tested was not seriously contaminated during transfer. Concentrated hydrochloric acid was poured over the ice to bring the temperature of the cooling bath to −20°, at which temperature it was maintained.

Both nitrogen tetroxide and freezing bath were frequently agitated. The *liquid* nitrogen tetroxide tem-

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[1] Presented before the Division of Cellulose Chemistry at the 110th Meeting of the American Chemical Society, September 1946, Chicago, Illinois.

[1a] Yackel and Kenyon, U. S. Patent 2,232,990 issued April 10, 1941.

[2] Yackel and Kenyon, THIS JOURNAL, 64, 121–127 (1942).

[3] Unruh and Kenyon, *ibid.*, 64, 127–131 (1942).

[4] Yackel and Kenyon, U. S. Patent Application 571,012.

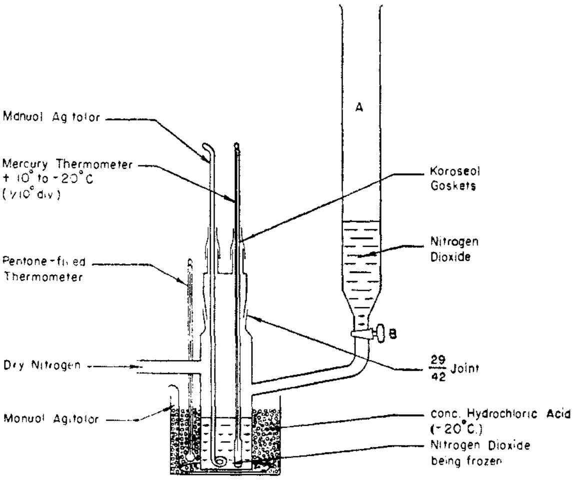

Fig. 2.—Cooling apparatus for nitrogen dioxide.

perature was read as a function of time. After about a quarter-inch layer of solid nitrogen tetroxide had formed about the periphery of the freezing chamber, subsequent freezing occurred very slowly, using the concentrated hydrochloric acid–ice-bath. The latter was then replaced by a Dry Ice–acetone-bath at −38 to −40° to provide more rapid freezing.

Results for three different samples of nitrogen peroxide are shown graphically in Fig. 3. The technical grade materials showed (a) no constant freezing temperature, (b) a wide freezing range and (c) lower freezing point than the purified material. The literature[5] gives −11.2° as the melting point, our purified material giving a freezing point in good agreement.

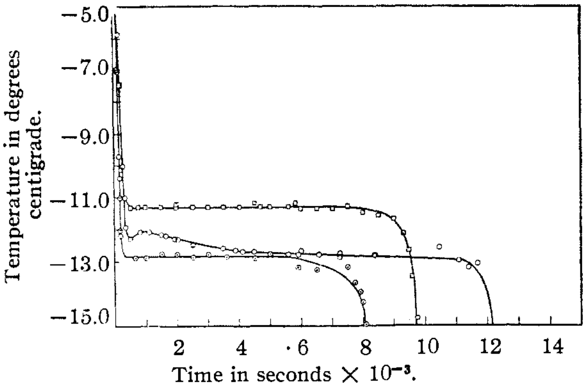

Fig. 3.—Cooling curves for nitrogen dioxide: □, purified substance; O, material as received from recovery plant; ⊙, commercial sample.

We use the terms, nitrogen dioxide and nitrogen tetroxide, or their chemical formulas interchangeably to mean the equilibrium mixture, $NO_2 \rightleftarrows N_2O_4$, which exists under the conditions of temperature and dilution employed.

Nitrogen trioxide (N_2O_3) gas, liberated from sodium nitrite by sulfuric acid, was dried[6] in a column of fused calcium nitrate, condensed in a tongue condenser using a slurry of solid carbon dioxide and trichloroethylene as refrigerant, then collected in a receiver surrounded by the same cooling agent. The system was well trapped to prevent contamination by atmospheric moisture. Pure material was removed from a small weight of solid nitrogen tetroxide which collected in the receiver by decanting the deep blue liquid while cold into another cooled reservoir.

Anhydrous Nitric Acid.—Two hundred grams of concentrated (68–70%) nitric acid was added dropwise to 500 g. of 94% sulfuric acid. This mixture was distilled in an atmosphere of carbon dioxide with protection against atmospheric moisture. The pale yellow fraction, b. p. 82–83°, was heated to 50° and carbon dioxide was bubbled through until the liquid was colorless. It was stored in brown, glass-stoppered bottles at 4–8°. The product was tested for purity by diluting a weighed sample to a known volume with water and titrating with phenolphthalein indicator, the acid being added to the base in determining the end-point. Results varied between 100.10 and 100.25% nitric acid by this method.

Oxidations Using Nitrogen Tetroxide–Carbon Tetrachloride Mixtures–No Nitric Acid Added

Procedure.—Ground cellulose (20-mesh) was used in these series. A weighed amount was placed in glass-stoppered pressure bottles and the mixtures of nitrogen tetroxide and carbon tetrachloride indicated in the tables were added. The tightly stoppered bottles were mechanically shaken at room temperature during the oxidation. Finely divided cellulose was used to secure as uniform penetration of the oxidant as possible. The room temperature variations were recorded during each series of oxidations and in the most extreme cases did not substantially exceed ±1°.

The resulting celluronic acids were mechanically separated from the oxidizing mixture, blown with air to remove volatiles, washed with carbon tetrachloride, and soaked in frequent changes of distilled water until the wash water was neutral to brom thymol blue indicator. The samples were air-dried to constant weight. Analytical samples were dried overnight at 55° *in vacuo* over phosphorus pentoxide. The carbon dioxide evolution method[7] and the calcium acetate method[8] for determining carboxyl contents have been previously described.

Variations in Ratio of Reactants.—In the first experiments the ratio of nitrogen dioxide to cellulose was varied from 3:1 to 12:1, the total weight of reactants being maintained at a constant value. This simultaneously changed the concentration of nitrogen dioxide in the oxidizing solution from a low value of 16.7% to a high value of 66.7% by weight. The reaction was followed by periodically re-

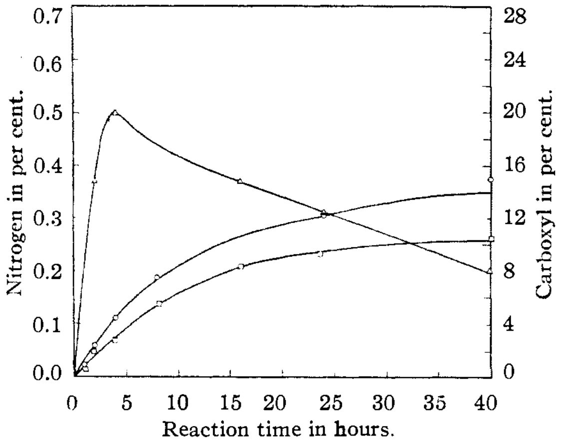

Fig. 4.—Oxidation of cellulose in nitrogen dioxide and carbon tetrachloride: ratio of liquids—nitrogen dioxide/carbon tetrachloride by weight 15/75; △, combined nitrogen; O, uronic acid; □, carboxyl by calcium acetate.

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[5] Yost and Russell, "Systematic Inorganic Chemistry," Prentice-Hall, New York, N. Y., 1944, p. 17.

[6] Mellor, "Modern Inorganic Chemistry," Longmans, Green and Co., Toronto, 1936, p. 645.

[7] Taylor, Fowler, McGee and Kenyon, This Journal, **69**, 342 (1947).

[8] McGee, Fowler and Kenyon, *ibid.*, **69**, 347 (1947).

TABLE I

TIME SERIES OF OXIDATION OF GROUND CELLULOSE: 5 G. CELLULOSE; 21.0 ± 0.5°

Wt. ratio NO_2/CCl_4	Analysis, wt.%	Time of oxidation, hours 1	2	4	8	16	24	40
15/75	Uronic acid carboxyl	0.84	2.37	4.41	7.52	8.66	12.23	15.05
	Calcium acetate carboxyl	2.3	..	2.7	5.5	8.4	9.2	10.5
	Nitrogen	0.32	0.37	0.50	0.31	0.37	0.31	0.20
30/60	Uronic acid carboxyl	1.78	3.52	7.01	10.37	13.52	15.82	14.68
	Calcium acetate carboxyl	5.4	1.9	5.6	10.1	...	16.0	15.5
	Nitrogen	0.33	0.73	0.48	0.42	0.36	0.31	0.23
45/45	Uronic acid carboxyl	2.48	5.14	12.82	21.17	20.82	23.03	24.31
	Calcium acetate carboxyl	1.0	2.8	10.6	10.2	18.3	19.3	23.8
	Nitrogen	0.35	0.31	0.61	0.58	0.42	0.43	0.14
60/30	Uronic acid carboxyl	2.31	5.20	13.57	20.68	23.75	24.20	...
	Calcium acetate carboxyl	0.5	3.4	11.6	19.1	23.6	21.8	23.4
	Nitrogen	0.34	0.48	0.71	0.67	0.31	0.17	0.17

moving samples over a total period of forty hours. The amount of oxidation in terms of per cent. of carboxyl by weight determined by the uronic acid method and the calcium acetate method are shown in Table I. The combined nitrogen (per cent. by weight) was determined by the DeVarda method. Figure 4 shows graphic presentation of data for 15/75 ratio.

Table II shows the results of similar experiments on using a wider range of variations in nitrogen dioxide/carbon tetrachloride and nitrogen dioxide/cellulose ratios.

TABLE II

OXIDATION OF GROUND CELLULOSE

Varying N_2O_4:CCl_4 ratio; varying N_2O_4:cellulose ratio; 16 hours reaction; temperature 21 ± 0.5°; 5 g. cellulose.

Liquid ratio = N_2O_4 g./CCl_4 g.	% N, by wt.	% Carboxyl by wt. Uronic acid	Calcium acetate
20/100	0.42	6.66	5.9
40/80	.53	...	8.3
60/60	.61	19.87	18.3
80/40	.73	21.48	23.4
100/20	.84	20.28	14.3
120/0	.87	18.75	15.3

The results obtained on using a constant nitrogen dioxide–cellulose ratio of 6:1 by weight while changing the concentration of nitrogen dioxide are tabulated in Table III.

TABLE III

OXIDATION OF GROUND CELLULOSE

Varying N_2O_4:CCl_4 ratio; constant N_2O_4:cellulose ratio; 16 hours reaction; temperature 21 ± 1°; 5 g. cellulose.

Liquid ratio = N_2O_4 g./CCl_4 g.	% N by wt.	% Carboxyl by wt. Uronic acid	Calcium acetate
30/30	0.32	21.10	18.0
30/60	.33	12.89	15.6
30/90	.35	9.32	9.8
30/120	..	7.68	7.6
30/150	.39	7.45	..
30/180	.40	7.02	6.4
30/210	.40	6.34	5.9
30/240	.39	5.93	5.4

A series of experiments in which the nitrogen dioxide-cellulose ratio was changed from 60:1 to 12:1 at constant nitrogen dioxide concentration gave the results shown in Table IV.

TABLE IV

OXIDATION OF GROUND CELLULOSE

Constant N_2O_4:CCl_4 ratio; varying N_2O_4:cellulose ratio; 16 hours reaction; temperature 21.5 ± 0.5°

Cellulose, g.	1:2 by wt. N_2O_4:CCl_4 soln., g.	% N	% Carboxyl by wt. Uronic acid	Calcium acetate
3	270	0.76	11.66	..
6	270	.50	11.54	11.5
9	270	.31	11.70	13.1
12	270	.29	14.11	13.6
15	270	.24	15.47	13.9

Oxidations Using Nitrogen Dioxide–Carbon Tetrachloride —Nitric Acid Added

Procedure.—In all of the following experiments, gauze was used instead of ground cellulose. In making the control runs where no nitric acid was added, the technique employed was that described in the previous section for ground cellulose. Experiments using nitric acid necessitated the following technique because of the limited solubility of the acid in the other reagents: The weighed amounts of nitric acid and carbon tetrachloride were placed in a pressure bottle and stirred. Usually two liquid layers were present. The weighed gauze sample was loosely inserted in the bottle above the liquids. The indicated amounts of liquid nitrogen dioxide were used to flush the gauze into the other reactants so that the gauze came into contact with the heterogeneous liquid system under as nearly constant conditions as possible. The stoppered pressure bottles were handled during the oxidations and the celluronic acids isolated as previously described.

Experiments in the presence of added nitrogen trioxide could not be run in bottles owing to high pressures generated. They were run in flasks equipped with stainless-steel condensers in which a refrigerant of Dry Ice–ethylene trichloride was placed. Little nitrogen trioxide escaped. The outlet was protected from atmospheric moisture. The liquid reactants, except nitrogen trioxide, were mixed in the flask and the gauze was added. The flask and contents, cooled to −20°, were placed on a balance, the liquid nitrogen trioxide was weighed in, and the flask was connected to the reflux. The reaction system was rapidly brought to room temperature and there maintained. Celluronic acids were isolated as previously described.

Throughout these series a standard ratio of reactants of 5:60:60:x was employed. Five parts of gauze, 60 parts of nitrogen dioxide, 60 parts of carbon tetrachloride, and x parts of nitric acid were chosen for correlation with previous practice and manipulative ease. x represents unit ratios from 0 to 7 inclusive. Ratios are on a weight basis. All experiments were at 25.0 ± 0.5°.

Effect of Added Nitric Acid on the Combined Nitrogen

Figures 5, 6 and 7 show the effect of varying amounts of added nitric acid on the combined nitrogen content, the carboxyl content by uronic acid method, and the carboxyl content by calcium acetate method, respectively, at various oxidation periods.

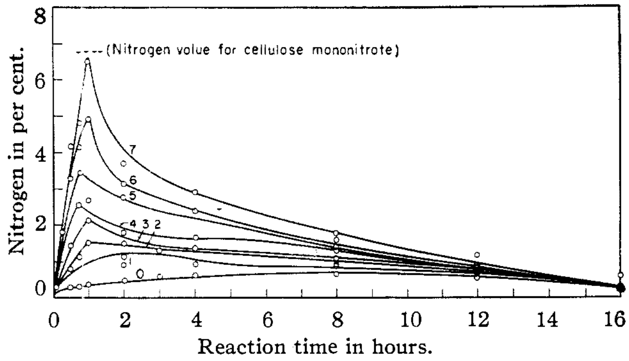

Fig. 5.—Nitration of cellulose with nitric acid in presence of nitrogen dioxide and carbon tetrachloride. Numbers on curves refer to parts of anhydrous nitric acid.

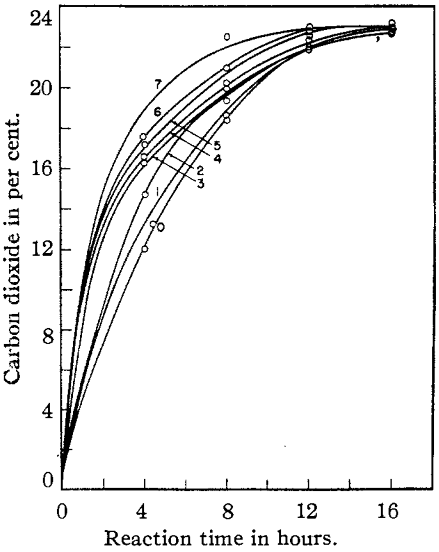

Fig. 6.—Uronic acid analysis of cellulose oxidized with nitric acid–nitrogen dioxide–carbon tetrachloride mixtures. Numbers on curves refer to parts of anhydrous nitric acid.

Optimum Nitration Time

The 5:60:60:x series, wherein $x = 7$, gave the highest intermediate nitrogen content. The time intervals were too great to fix accurately the maximum of the curve so a series at 5:60:60:7 was run with very small time increments. The results shown in Fig. 8 confirm the maximum for this ratio at about a one-hour reaction period.

Nitration of Cellulose by Nitric Acid in Nitrogen Dioxide–Carbon Tetrachloride Mixtures

In the data of Fig. 5 the maximum nitration content increased with increasing concentrations of nitric acid. It appeared of interest to determine whether the nitration at a one-hour reaction period would continue to increase with still greater nitric acid concentrations. The results are shown in Fig. 9.

Nitration of Cellulose by Nitric Acid without Nitrogen Dioxide

The experiments described in Table V were designed to determine the effect of anhydrous nitric acid in absence of nitrogen dioxide. Comparative runs are included using nitrogen dioxide with and without added nitric acid. Certain of the data are shown graphically in Fig. 10.

Investigation of the Denitration–Oxidation Process

The experiments tabulated in Table VI were designed to show the effect of various reactants on the denitration–oxidation step. The gauze was first nitrated by using a 5:60:60:7 ratio. After a one-hour reaction at room temperature, the gauze was worked up as described for celluronic acid. It contained 5.7% nitrogen.

Data from Table VI indicated that nitric acid may catalyze the denitration–oxidation process. The series of Table VII were run for confirmation.

Iodination of Cellulose Mononitrate

The iodination of cellulose mononitrate (containing 6.73% of nitrogen and prepared as previously indicated) was performed in the following way:

Five grams (0.03333 mole) of sodium iodide (0.22% moisture) was dissolved in 200 cc. of Eastman Kodak Co. acetonylacetone (no moisture by Fischer reagent). Two grams (0.00971 mole) of cellulose mononitrate was added to the solution and the mixture thoroughly shaken. The cellulose mononitrate swelled enormously. After thorough mixing, the flask was placed under a reflux condenser protected by a drying tube. The temperature of the solution was kept between 130 and 135° for sixteen hours. The sample was filtered, washed with ethanol, and leached in deci-normal sodium thiosulfate solution for eight hours. The material was washed with more of the thiosulfate solution on a glass filter, washed with many changes of distilled water, and dried to constant weight over phosphorus pentoxide. Analyses for nitrogen by the DeVarda technique, and for iodine, have been summarized with calculations similar to those employed by Murray and Purves[9] (Table VIII).

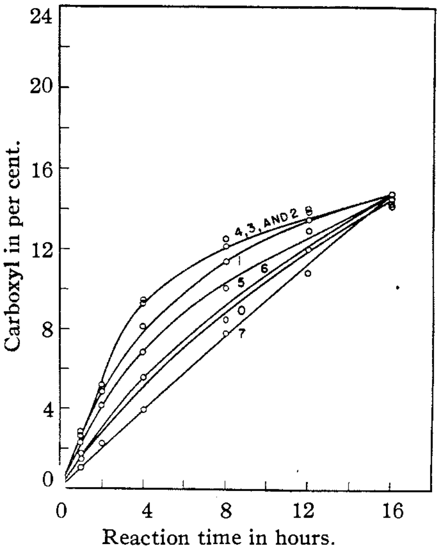

Fig. 7.—Carboxyl by calcium acetate for cellulose oxidized with nitric acid–nitrogen dioxide–carbon tetrachloride mixtures. Numbers on curves refer to parts of anhydrous nitric acid.

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(9) Murray and Purves, This Journal, 62, 3194 (1940).

TABLE V

REACTION OF CELLULOSE WITH ANHYDROUS NITRIC ACID

5 PARTS CELLULOSE

Anhydrous HNO_3	CCl_4	N_2O_4	Reaction time, hr.	Wt., % N	Wt. % COOH Uronic acid	$Ca(OAc)_2$
3.5	120		1	4.1	10.12	0
7.0	120		1	5.4	13.23	0
10.5	120		1	7.8	17.28	0
14.0	120		1	10.6	17.13	0
7.0	120		2	7.2	14.40	0
7.0	120		4	7.2	16.50	0
7.0	120		6	7.6	15.65	0
7.0	120		8	6.7	14.45	0
	60	60	2	0.58	11.94	8.66
	60	60	4	0.78	16.97	16.25
	60	60	6	0.76	19.33	18.75
	60	60	8	0.67	19.76	19.70
7.0	60	60	2	2.30	15.87	3.81
7.0	60	60	4	1.90	17.11	8.18
7.0	60	60	6	0.58	18.92	15.30
7.0	60	60	8	0.80	20.27	15.40

TABLE VI

DENITRATION OF NITRATED GAUZE (5.7% N)

Nitrated gauze	Ratio of reactants by wt.				Reaction time, hours	Wt.% N	Wt. % carboxyl	
	CCl_4	N_2O_4	N_2O_5	HNO_3			Uronic acid	Calcium acetate
5	60		60	7	4	4.1	15.73	0.56
5	60		60	7	8	1.3	19.03	7.38
5	60	60		1	20	0.61	25.03	13.17
5	60	60		2	20	.37	25.26	13.86
5	60	60		3	20	.32	25.60	13.74
5	60	60		6	20	.23	25.16	14.00
5	60		60		5	6.1	14.02	1.60
5	60		60		7, 5	6.2	14.75	1.72
5	60	60			16	3.4	21.92	8.76
5	60			7	16	7.9	19.57	0.90
Original nitrated gauze	..	..	..	...	..	5.7	10.92	0.58

TABLE VII

DENITRATION–OXIDATION OF NITRATED GAUZE (6.5% N)

5:60:60:x RATIO

Reaction time, hours	$x = 0$			$x = 7$		
	% N	Carboxyl Uronic acid	Carboxyl $Ca(OAc)_2$	Wt. % N	Wt. % carboxyl Uronic acid	Wt. % carboxyl $Ca(OAc)_2$
2	2.50	18.54	5.89	3.10	19.92	4.81
4	2.00	18.42	6.95	1.00	20.35	7.27
6		19.27	7.77	0.40	21.48	9.55
8	1.70	19.62	9.19	.38	23.21	17.90

TABLE VIII

Original nitrate		N, %	6.73
		Moles	0.994
Iodinated nitrate	Iodine	I, %	33.54
		Moles	0.605
	Nitrate	N, %	0.08
		Moles	0.013
Moles of original nitrate, %		Replaced by I	60.9
		Remaining	1.32
		Lost	37.72

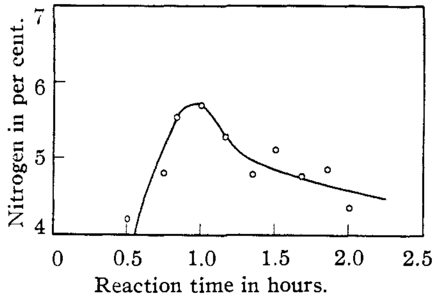

Fig. 8.—Reaction time to produce highest nitration with ratio of reactants 5:60:60:7.

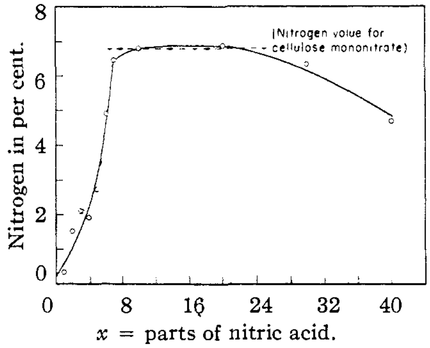

Fig. 9.—One-hour oxidations of cellulose gauze using ratio of reactants 5:60:60:x, where x = parts of anhydrous nitric acid.

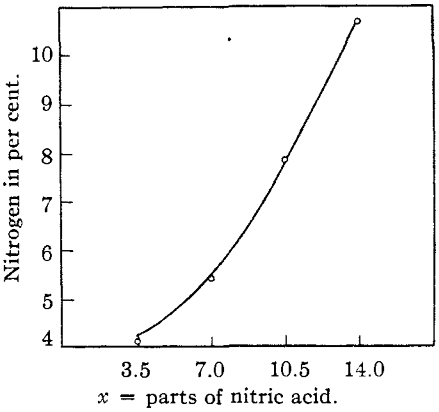

Fig. 10.—One-hour oxidations of cellulose using 5 parts cellulose, 120 parts carbon tetrachloride, and x parts of anhydrous nitric acid.

Discussion

The interpretations of the extent of oxidation are offered with some reservations, for the carboxyl contents obtained with the carbon dioxide evolution method may be somewhat high owing to combined nitrate groups[7] while the carboxyl values from the calcium acetate method are believed to be slightly low.[8] However, the data are sufficiently precise to show the course of the oxidation.

In the experiments conducted in the absence of added anhydrous nitric acid, a number of pertinent generalizations become apparent. At a constant reaction time of sixteen hours the nitrogen dioxide/cellulose ratio at constant oxidant concentration has little effect on the degree of oxidation though increase of the ratio increases the combined nitrogen content (Table IV). At constant oxidant/cellulose ratio the degree of oxidation increases severalfold as the concentration of oxidant in the carbon tetrachloride solution is increased though the combined nitrogen content changed only slightly (Table III). In these series the carboxyl contents of both analytical methods were in fair agreement. Simultaneous variation of both oxidant concentration and oxidant/cellulose ratio (Table II) caused changes of both degree of oxidation and nitrogen content which are compatible with the previous series in which a single factor was varied.

The most significant result from the standpoint of the mechanism is evident in Table I and Fig. 4, where the nitrogen value reached maxima after a relatively short reaction time and then more slowly decreased to very low amounts. It appears evident that the cellulose first partially nitrates and then denitrates in the course of the oxidation. With a fixed oxidation time (Table IV), the amount of combined nitrogen varied inversely as the amount of cellulose, because the source of nitration—either the nitrogen peroxide or a substance produced from it—remained constant as the amount of cellulose was increased. Oxidation of hydroxyl groups to carboxyl forms water as a by-product which readily reacts with nitrogen dioxide to generate anhydrous nitric acid. This consideration led to experiments to evaluate its role in the oxidation mechanism.

When varying amounts of anhydrous nitric acid are added to a carbon tetrachloride–nitrogen dioxide–cellulose oxidation mixture, the rapid nitration of the cellulose may attain the value for cellulose mononitrate, as shown in Fig. 5. Then, in all cases examined, the ester is converted at a much slower rate by a step (or series of steps), now not entirely clear, to celluronic acid. While the carboxyl values by carbon dioxide evolution were in the early stages substantially proportional to the amount of nitric acid added (Fig. 6), the free carboxyl values obtained by the calcium acetate method were less regular with respect to nitric acid concentration (Fig. 7). Both methods of analysis produced values which converge at the end of sixteen hours reaction time, the uronic acid carboxyl at about 23% and the calcium acetate carboxyl at approximately 14.5%. The marked discrepancy between the two values may be attributed to inter- or intramolecular dehydration[8] in the presence of the nitric acid (see also Table V).

More exact determination of some of the factors involved in the nitration process seemed desirable. The reaction time of one hour is seen from Fig. 8 to represent, within rather narrow limits, the point at which maximum nitration of the cellulose occurs when the ratio of reactants and diluent is 5:60:60:7. The addition of more than seven parts of anhydrous nitric acid did not produce in one hour combined nitrogen values in excess of that for cellulose mononitrate (Fig. 9). From one-hour "oxidations" as control experiments wherein nitrogen tetroxide was omitted (Table V), it is evident (Fig. 10) that the presence of the latter reagent prevents nitration of the cellulose beyond the value for a mononitrate, since omission of this substance resulted in greatly enhanced nitration. The cellulose treated in absence of nitrogen tetroxide showed no detectable carboxyl by the calcium acetate method. This further corroborates the role of nitrate groups in producing spurious uronic acid values.[7]

We suggest, from the above, that the oxidation of cellulose with nitrogen tetroxide involves at least two steps, the first of which is nitration. It is well known to be virtually impossible to prepare an anhydrous cellulose as powerful desiccants ultimately begin to remove "water of constitution" from cellulose, so we may believe that some nitric acid will be present in any nitrogen tetroxide scheme for oxidizing cellulose. Thus

$$2N_2O_4 + H_2O \longrightarrow 2HNO_3 + N_2O_3 \qquad (1)$$

$$(C_6H_{10}O_5)_x + xHNO_3 \longrightarrow (C_6H_9ONO_2)_x + xH_2O \qquad (2)$$

$$(C_6H_9ONO_2)_x \xrightarrow{N_2O_4} (C_5H_8COOH)_x \qquad (3)$$

The experiments of Table VI show the effects of various substances on the rate at which cellulose mononitrate was decomposed to celluronic acid. Nitrogen trioxide appears almost completely to inhibit the step(s) of conversion from nitrate ester to carboxyl group. The presence of nitric acid together with nitrogen tetroxide results in rapid denitration–carboxylation. The apparently catalytic effect of nitric acid is shown by the data of Table VII. The combined nitrogen decreases more rapidly, the calcium acetate carboxyl values rise more rapidly and to a higher ultimate value, while the uronic acid carboxyl (the least reliable criterion of the three for this purpose) rises slightly faster in the presence of nitric acid. We conclude that the presence of nitric acid in the oxidation mixture catalyzes—or may be the reactive agent in—conversion of nitrate ester to carboxyl group, so equation (3) may be restated

$$(C_6H_9ONO_2)_x \xrightarrow[(HNO_3)]{N_2O_4} (C_5H_8COOH)_x \qquad (4)$$

The data presented in Table VIII show that practically all of the nitrate groups are replaced or hydrolyzed by using the experimental method of Irvine and Rutherford.[10] If we interpret our results in accordance with the published data on the glucose nitrates, it appears that practically all of the nitrate groups are present as esters of the primary hydroxyl and the small amount remaining after sodium iodide treatment represents a

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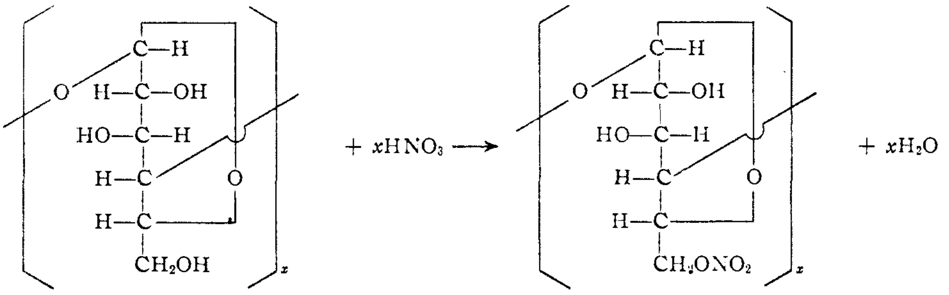
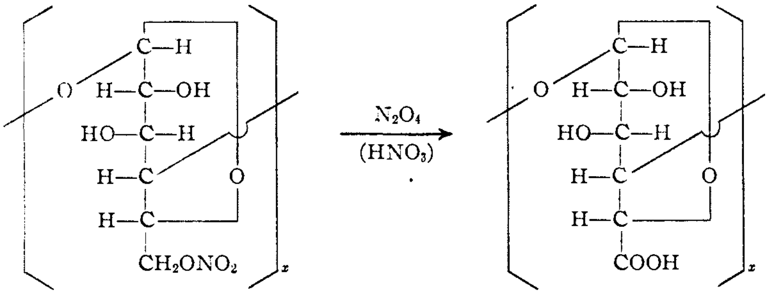
[10] Irvine and Rutherford, This Journal, 54, 1491 (1932).

very small nitration of secondary hydroxyl groups. This interpretation must not at present be considered as final proof. However, specificity of the nitration reaction with respect to the primary positions would explain why the oxidation yields polyanhydro-uronic acid groups. Using the interpretation that our polyanhydro-D-glucose "mononitrate" involves substantially only the C_6 position, we may modify equations (2) and (4) above as follows



(5)



(6)

It is very difficult to prepare cellulose derivatives (except the tri-derivatives) having substituent groups selectively placed on specific carbon atoms. However, the maximum nitrogen contents of the cellulose nitrates obtained in the presence of nitrogen dioxide and their behavior when treated with iodine are compatible with the formation of a cellulose 6-mononitrate. The role of the dioxide in limiting nitration is remarkable and should be further investigated.

The mechanism outlined may explain the general mechanism of the oxidation of hydroxyl groups in other organic compounds. Aliphatic alcohols, like cellulose, yield alkyl nitrates when reacting with nitric acid. Unless urea is added to destroy nitrous acid (or probably nitrogen oxides) present in the nitric acid or formed by degradative side reactions, the alcohol is so violently oxidized that explosions may occur.[11]

We suggest that the aliphatic alcohols are first nitrated by nitric acid and the explosive reaction is the very rapid oxidation–denitration step induced by the nitrogen oxides. It has been shown[12] that the higher aliphatic primary alcohols are oxidized by nitrogen dioxide, either in the liquid or vapor phase, to the corresponding acid in good yield. In this case the rapid denitration–oxidation step is controlled.

Summary

1. The rate of oxidation of cellulose has been studied by using various ratios of the reactants, cellulose, nitrogen tetroxide and carbon tetrachloride diluent.

2. In the absence of added nitric acid, the combined nitrogen rises in early stages of oxidation and then slowly decreases. The cellulose: nitrogen tetroxide ratio was inversely proportional to the amount of combined nitrogen.

3. In the presence of added nitric acid, considerable nitration of the cellulose occurs as a preliminary step in the oxidation process.

4. The presence of nitrogen tetroxide limits the nitration reaction to the analytical value for a cellulose mononitrate.

5. The nitration appears substantially limited to the primary hydroxyl.

6. The oxidation step is the result of the oxidative-denitration of the preliminary nitrate. Nitrogen tetroxide is involved in the denitration and nitric acid appears catalytic.

7. The small amounts of residual combined nitrogen usually found in celluronic acids may be the result of nitration of secondary hydroxyl groups.

8. This mechanism of oxidation has not been previously elucidated. It may underlie many of the oxidations of hydroxyl-containing organic compounds using nitric acid as the oxidant.

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(11) N. V. Sidgwick. "The Organic Chemistry of Nitrogen," revised by T W. J. Taylor and W. Baker, Oxford, Clarendon Press, 1937, p. 7.

(12) G. V. Heyl and W. O. Kenyon, U. S. Patent 2,298,387, issued Oct. 13, 1942.