PREPARATION OF FIBROUS CELLULOSE FORMATE BY THE ACTION OF THIONYL CHLORIDE IN *N,N*-DIMETHYLFORMAMIDE*

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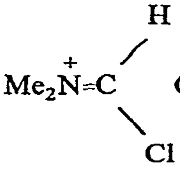
(Received September 16th, 1971)

ABSTRACT

Cotton cellulose yarn, either in the untreated state, or altered by swelling pretreatments involving mercerization or solvent-exchange, or both, reacts readily with solutions of thionyl chloride in *N,N*-dimethylformamide at room temperature. Subsequent hydrolysis produces cellulose formate as the major product; this derivative is presumably formed *via* reaction of the cellulose with the iminium salt,  $\mathrm{Me_2\overset{+}{N}{=}C(H)(Cl)\ \overset{-}{Cl}}$. The minor products are a sulfurous acid monoester of cellulose and a chlorodeoxycellulose.

The reaction variables studied were the effect of (*a*) preswelling the cellulose in *N,N*-dimethylformamide, (*b*) the reaction time, (*c*) the concentration of thionyl chloride, and (*d*) the moisture content of the cotton prior to preswelling and reaction. The effect of various pretreatments on the type and rate of reaction which the cotton undergoes was also determined. The stability of the formyl group and of the sulfurous acid monoester group to hot water and to dilute ammonium hydroxide, as well as the tensile properties of yarns treated with thionyl chloride and *N,N*-dimethylformamide, were investigated.

INTRODUCTION

Previous work in these laboratories[1] and by Polyakov and Rogovin[2] has shown that a chlorodeoxycellulose can be prepared by the reaction of thionyl chloride in *N,N*-dimethylformamide with mercerized, solvent-exchanged cellulose. When conducted at room temperature, the reaction to form the chlorodeoxy derivative presumably proceeds through the chlorosulfite intermediate, because moderate proportions

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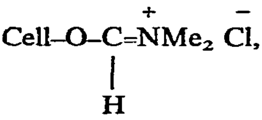
*Presented, in part, at the 161st National Meeting of the American Chemical Society, Los Angeles, California, March 28–April 2, 1971.

of sulfur are still retained, even after washing with dilute ammonium hydroxide (which removes most of the sulfurous acid monoester groups). However, if the cellulose is washed with water only, it has, in addition to appreciable contents of sulfur and chlorine, carbonyl absorptions in its i.r. spectrum that are typical of cellulose formate.

With unmercerized cotton cellulose, the chlorosulfite intermediate must play a minor role, as, after water-washing and air-drying, comparatively little sulfur and chlorine were detected in the modified cellulose, relative to the degree of substitution (d. s.) of the cellulose formate obtained. Therefore, a different intermediate, namely  $\mathrm{Cell{-}O{-}\underset{\displaystyle H}{\underset{|}{C}}{=}\overset{+}{N}Me_2\ \overset{-}{Cl}}$, must, on hydrolysis, yield cellulose formate.

With respect to the two intermediates mentioned, the effect of the physical state of the cellulose, the concentration of thionyl chloride, and the reaction time are discussed. Also, the role of water in the hydrolysis of the cellulose iminium intermediate, and the importance of preswelling in *N*,*N*-dimethylformamide, are noted. The tensile properties of the resultant cellulose formate are listed; elemental analyses were made, so that the distribution of the various derivatives formed under particular reaction-conditions could be determined.

EXPERIMENTAL

The cellulose was loose-twist, 12/3 (tex-151), Deltapine, cotton yarn purified by kier boiling. Thionyl chloride, *N*,*N*-dimethylformamide (DMF), and 90% formic acid were reagent-grade, commercial materials.

A typical treatment consisted in immersion of the untreated, kiered yarn in an excess of DMF for 5–60 min at 25°, followed by shaking with 2–20% thionyl chloride in DMF at a ratio of 40 g of solution per g of cotton for 10 min–6 h at 25°. The yarn was subsequently washed with DMF (three times), with ice water until the pH of the washings was 4 or higher, and with tap water for 30 min, and then air-dried.

Modifications of this procedure consisted of (*1*) predrying the untreated cotton at 105–110° prior to immersion in DMF, (*2*) adding small amounts of DMF and distilled water to the reaction mixture during the course of shaking, or (*3*) conducting the same procedure on various physically modified or pretreated cotton yarns. Various pretreated yarns included those (*a*) solvent-exchanged with 95% ethanol and then benzene; (*b*) mercerized, washed, dried, and solvent-exchanged with 95% ethanol and then benzene; (*c*) mercerized, washed, and solvent-exchanged with 95% ethanol and then benzene; and (*d*) mercerized, washed, and dried. These modifications are noted in the footnotes to Tables II and IV.

The procedure for preparing cellulose formate by use of 90% formic acid was that of Rowland and Pittman[3].

The stability of the cellulose formates to hot water was investigated by boiling a skein in distilled water for 1 h, washing it briefly with cold distilled water, and air-drying.

Elemental analyses for chlorine and sulfur were performed by a commercial laboratory, and the formyl content of the cellulosic product (in some cases, corrected for the presence of sulfurous acid ester groups) was determined by the modified Eberstadt method described in ASTM D-871-63. Infrared (i.r.) spectra were recorded on a Perkin–Elmer Model 137B Infracord spectrophotometer* for pellets of the cellulose derivative in potassium bromide.

The breaking strength, elongation-at-break, and tenacity of the yarns were determined by ASTM method D-2256-64T. Energy-to-rupture values were obtained by using an automatic integrator attached to an Instron tester*.

RESULTS AND DISCUSSION

Effect of preswelling time in N,N-*dimethylformamide, and of reaction time, on conversion into cellulose formate.* — The reaction of thionyl chloride in DMF at room temperature with untreated cellulose yarn produces cellulose formate primarily. However, preswelling of the untreated cotton is necessary in order to obtain appreciable conversion into this derivative. For example, kiered yarn shaken for 1 h with 5 or 10% thionyl chloride in DMF, and washed by the procedure described in Table I, had a weight gain of only 1.4%, and exhibited little carbonyl absorption in its i.r. spectrum. In contrast, preswelling of the untreated yarn for 5 min in DMF prior to reaction, and repetition of the foregoing procedure, with 5.5% thionyl chloride,

TABLE I

EFFECT OF PRESWELLING TIME AND REACTION TIME ON THE CONVERSION OF CELLULOSE INTO CELLULOSE FORMATE

Preswelling time in DMF (min)	*Reaction time (min)*[a]	*Gain in wt. (%)*	*Apparent d.s. by formate*[b]	*Apparent d.s. by formate*[c]
5	10	3.9	0.23	0.22
	60	5.0	0.29	0.25–0.41
	180	7.9	0.46	0.37–0.46
30	10	3.5	0.20	0.21–0.22
	60	4.5	0.26	0.27–0.29
	180	5.9	0.34	0.33
60	10	3.6	0.21	0.18–0.20
	60	5.6	0.32	0.25–0.30
	180	6.3	0.36	0.34–0.35

[a] After immersion in DMF, all yarns were centrifuged for 1 min, and then allowed to react with 5.5% thionyl chloride in DMF (bath ratio of 40 g of solution/g of cotton) for the times listed, at 25°, washed with DMF, ice water, tap water for 30 min, and air-dried. [b] Calculated from gain in weight of yarns. [c] Calculated from total amount of alkali consumed in the Eberstadt method.

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*Use of the name of a company or product does not imply approval or recommendation of the product by the Department to the exclusion of others that may also be suitable.

resulted in a weight gain of 5.0% and an intense carbonyl absorption in the i.r. spectrum of the product.

The function of the DMF is probably twofold: (*a*) it increases the accessibility of the cellulose fibers by acting as a swelling agent, and thereby increases the extent of reaction of the hydroxyl groups with the iminium salt, and (*b*) it acts as a carrier or solvent for the iminium salt, and consequently increases the diffusion of this salt into the more accessible reaction-sites of the fiber.

The effect of preswelling time in DMF on the resultant gain in weight and extent of conversion of untreated cellulose into cellulose formate was investigated; the results are given in Table I. A comparison of untreated yarns treated with 5.5% thionyl chloride in DMF for the same reaction times, but for different preswelling times in DMF, shows that the preswelling time is not a variable, because, for a given reaction time, weight gains and d.s. (calculated by titration with base) are within experimental error of each other.

Conversely, the preswelling time was held constant, and the reaction time was varied. With a preswelling time of 5 min, the weight gains doubled as the time was increased eighteenfold. The d.s. of the cellulose formate (determined by titration) was in the range of 0.22–0.46. With different preswelling times (0.5 and 1 h), similar trends in the weight gain and d.s. were noted. At longer reaction times, values determined by titration were slightly lower than those derived from the weight gains; this result may be attributable to the formation of chlorodeoxycellulose.

Effect of concentration of thionyl chloride on conversion into cellulose formate. — The effect of the concentration of thionyl chloride on the extent of conversion into cellulose formate was also investigated; the preswelling time was held constant at 5 min, and the reaction time at 1 h. The results are given in Table II.

Progressively greater gains in weight were observed on increasing the concentration of the thionyl chloride from 2 to 10%; at higher concentrations (15 and 20%),

TABLE II

EFFECT OF CONCENTRATION OF THIONYL CHLORIDE ON CONVERSION OF CELLULOSE INTO CELLULOSE FORMATE

Thionyl chloride (%)[a]	*Gain in wt.* (%)	*Apparent d.s. by formate*[b]	*Apparent d.s. by formate*[c]
2	2.0	0.12	0.12
5.5	4.0	0.23	0.21
10	5.6	0.32	0.31
10	5.8	0.34	0.26–0.28
15	6.5	0.38	0.31–0.32
20	7.8	0.45	0.37–0.38

[a] After a 5-min immersion in DMF, all yarns were centrifuged for 1 min, and then allowed to react for 1 h with thionyl chloride, at the concentration listed, at 25° (bath ratio of 40 g of solution/g of cotton), washed with DMF, ice water, tap water for 30 min, and air-dried. [b] Calculated from gain in weight of yarns. [c] Calculated from total amount of alkali consumed in the Eberstadt method.

TABLE III

EFFECT OF MOISTURE IN THE CELLULOSE ON THE CONVERSION INTO CELLULOSE FORMATE

Preswelling time in DMF (min)	*Reaction time (min)*[a]	*Gain in wt. (%)*	*Apparent d.s. by formate*[b]	*Apparent d.s. by formate* [c]
5	10	1.4	0.08	0.05
	60	1.9	0.11	0.07
	180	1.4	0.08	0.05
60	60	1.2	0.07	0.08
5	60+60[d]	0.6	0.035	0.03
	60+60[e]	1.2	0.07	0.05

[a]After dehydration at 115° for 30 min followed by immersion in DMF, yarns were centrifuged for 1 min, allowed to react with 5.5% thionyl chloride in DMF for times listed, at 25° (bath ratio of 40 g of solution/g of cotton), washed with DMF, ice water, tap water for 30 min, and air-dried. [b]Calculated from gains in weight of yarns. [c]Calculated from total amount of alkali consumed in the Eberstadt method. [d]Water (0.2 g) in DMF (50 ml) was added to the mixture after the first hour. [e]Water (1.2 g) in DMF (50 ml) was added to the mixture after the first hour.

the weight gains increased somewhat more slowly. With concentrations of 10% thionyl chloride or less, the d.s. determined by titration and that observed from the weight gains were in good agreement; however, at higher concentrations (15 or 20%), the d.s. from titration was significantly lower than that based on the weight gain. This result is probably attributable to the formation of chlorodeoxycellulose.

Effect of removal of moisture on the conversion into cellulose formate. — As previously mentioned, preswelling in DMF was found to be a prerequisite for obtaining substantial conversion of untreated cotton into cellulose formate. In addition to this requirement, the cellulose must contain its normal content of moisture in order that it may react in any degree with the thionyl chloride in DMF, even if the cotton is swollen in DMF prior to the reaction.

As shown in Table III, untreated cellulose yarns heated for 30 min at 110–115° before immersion in DMF failed to show any appreciable weight gains when shaken with 5.5% thionyl chloride in DMF for various periods of time. The highest gain in weight recorded was 1.9%; titration gave a calculated d.s. of only 0.07. Addition of water to the reaction mixture after the first hour also failed to cause an increase in the weight during a subsequent period of one hour.

Removal of the water in the cellulose by heat may collapse the fiber, and make it less accessible to the reactants. Also, the water in the unmodified cellulose may react with the cellulose iminium intermediate much faster than water that would have to diffuse in from outside the fiber, and may thereby facilitate formation of cellulose formate. In either case, the moisture present in the cotton fiber is necessary in order that appreciable reaction may occur under comparable experimental conditions.

Effect of pretreatments on conversion into cellulose formate and other derivatives. — All the parameters already discussed were investigated only on untreated cotton yarn and on untreated cotton that had been heated to remove moisture. In order to detect differences in the rate of reaction to form cellulose formate, as well as to ascertain the efficiency of such competing reactions as the formation of chlorodeoxycellulose and the sulfurous acid monoester of cellulose, various pretreatments of cotton were investigated with respect to rate and type of reaction.

The various treatments investigated were the following: (*a*) untreated cotton (U), (*b*) untreated cotton, solvent-exchanged with 95% ethanol, and then benzene (SE), (*c*) cotton mercerized in 23% sodium hydroxide, washed, and dried (MD), (*d*) cotton mercerized in 23% sodium hydroxide, washed, dried, and solvent-exchanged with 95% ethanol and then benzene (MDSE), and (*e*) cotton mercerized in 23% sodium hydroxide, washed, and solvent-exchanged with 95% ethanol and then benzene (MSE). The resultant yarns were centrifuged to remove the excess of benzene (when applicable), immersed in DMF for 1 h, recentrifuged, allowed to react with 5.5–10% thionyl chloride in DMF, and washed by the procedure indicated in Table IV.

TABLE IV

EFFECT OF PRETREATMENTS OF COTTON ON THE PRODUCTS FORMED FROM THE REACTION OF CELLULOSE WITH THIONYL CHLORIDE AND *N*,*N*-DIMETHYLFORMAMIDE

Pretreatment used	*Reactants*[a]	*Gain in wt.* (%)	*S* (%)	*Cl* (%)[b]	*Apparent d.s. by formate*[c]	*Apparent d.s. by formate*[d]
Mercerized, washed, solv. exchanged to 95% EtOH, then benzene	5.5% $SOCl_2$	8.1			0.68	
	10% $SOCl_2$	16.6	3.20	0.95	1.14	0.70
Mercerized, washed, dried, solv. exchanged to 95% EtOH, then benzene	5.5% $SOCl_2$	1.3			0.29	
	10% $SOCl_2$	7.2	1.02	0.30	0.50	0.38
Solv. exchanged to 95% EtOH, then benzene	5.5% $SOCl_2$	5.0			0.33	
None	5.5% $SOCl_2$	5.3	0.79	0.39	0.31	0.22
None	90% HCOOH[e]	−0.7			0.19	0.19

[a]All yarns were centrifuged, when necessary, to remove benzene, and then allowed to stand in an excess of DMF for 1 h, centrifuged for 1 min, allowed to react in the above solutions (in DMF) for 1 h at 25°, washed with DMF, ice water, and then tap water (for 30 min), and air-dried. Bath ratio was 40 g of solution/g of cotton. [b]Uncorrected for moisture and ash (blanks indicate that analyses were not performed). [c]Calculated from total amount of alkali consumed in the Eberstadt method. [d]Recalculated by subtracting the amount of alkali consumed in the side reaction (formation of cellulose sulfurous acid ester). [e]For 18 h at 26° with 100 ml of formic acid/g of cotton, by method of Ref. 2.

In terms of overall reaction, the MSE-treated yarn had the highest gain in weight (8.1%), followed by untreated cotton (5.3%), SE-treated yarn (5.0%), MDSE-treated yarn (1.3%), and MD-treated yarn (no weight gain). The d.s. determined by titration were in approximately the same order, namely, 0.68, 0.31, 0.33, 0.29, and 0.00. However, these values of d.s., as well as those in Tables I–III, do not taken into account the possible presence of –O–S(O)OH groups (which would also consume alkali).

To obtain more-complete information, yarns having the respective history designated U, MSE, and MDSE were treated with 10% thionyl chloride in DMF for 1 h, and the sulfur, chlorine, and formyl content of each product was determined. The S/Cl ratio was remarkably constant for all three, the greatest proportion of chlorodeoxycellulose and of the sulfurous acid monoester of cellulose being formed by the MSE pretreatment. This result was not unexpected, as previous work in these laboratories on the preparation of chlorodeoxycellulose had indicated that this pretreatment gave optimal reaction[1]. What *was* surprising, however, was that a considerable proportion of cellulose formate was also formed by use of an MSE pretreatment, giving a formate d.s. of 0.70 (after correction for sulfurous acid groups). The same trend was noted in the MDSE samples and the U samples, namely, that cellulose formate is the major product, followed, in order, by the sulfurous acid monoester of cellulose and by chlorodeoxycellulose.

The i.r. spectra of the various treated yarns are given in Fig. 1. Spectra A through C, which correspond to pretreatments MSE, MDSE, and U, respectively,

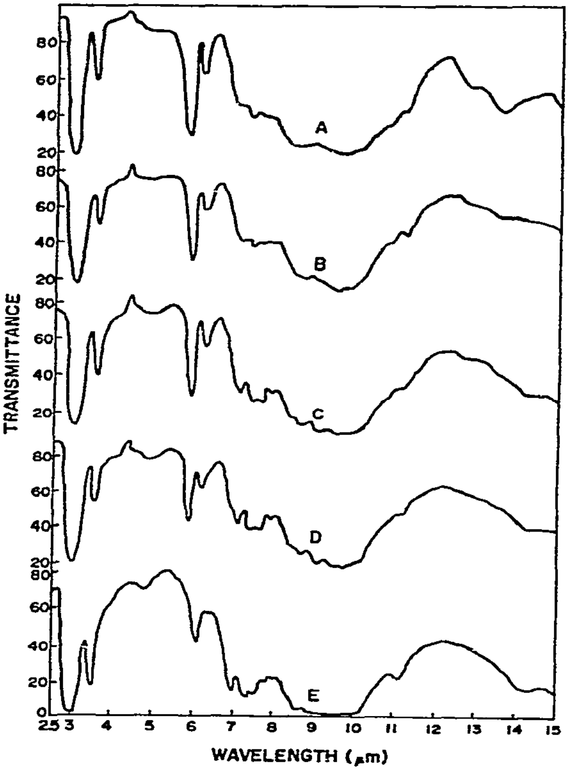

Fig. 1. I.r. spectrum of 12/3 kiered, cotton yarns: (A) mercerized, washed, solvent-exchanged, immersed in DMF for 1 h, treated for 1 h at 25° with 10% thionyl chloride in DMF, (B) mercerized, washed, dried, solvent-exchanged, immersed in DMF for 1 h, treated for 1 h at 25° with 10% thionyl chloride in DMF, (C) immersed in DMF for 1 h, treated for 1 h at 25° with 5.5% thionyl chloride in DMF, (D) immersed in 90% formic acid for 18 h at 26°, and (E) no treatment.

all exhibit, at 5.8-5.9 μm, the characteristic carbonyl stretch attributed to the formyl group.

Cellulose formate was also prepared by the method described by Rowland and Pittman[3]; its i.r. spectrum and its stability to water and dilute ammonium hydroxide were compared to those of yarns treated by the thionyl chloride–DMF method.

As may be seen from Fig. 1 (C and D), the spectra of untreated yarn treated with 5.5% thionyl chloride in DMF and of untreated yarn treated with 90% formic acid by the method of Rowland and Pittman[3] were practically identical. The treatment to give the material affording spectrum C was chosen because the product had the same d.s. as the cellulose formate prepared with 90% formic acid.

The stability of the cellulose formates prepared by both methods was investigated by boiling each yarn separately for 1 h in distilled water, briefly washing with cold distilled water, centrifuging to remove the excess of water, and allowing it to air-dry. The cellulose formate prepared by the formic acid method originally had a d.s. of 0.19, and this value was lowered to 0.14 after the treatment with boiling water; similarly, the cellulose formate prepared by reaction of untreated cotton with 5.5% thionyl chloride in DMF had a d.s. of 0.22, lowered to 0.15 after treatment with boiling water. This result showed that the two cellulose formates were of comparable stability. Also of interest was the fact that the yarn treated with thionyl chloride showed very little change in chlorine or sulfur content (Cl, 0.39 to 0.29; S, 0.79 to 0.70) after boiling in water. Evidently, the sulfurous acid monoester of cellulose is more stable than cellulose formate to the action of boiling water.

Several of the yarns described in Table IV were shaken for 1 h with 3% aqueous ammonium hydroxide, washed with tap water for 30 min, and air-dried. Without exception, the formyl group was completely hydrolyzed off. Most of the sulfurous acid ester groups were also removed, as shown by analysis of the yarn given the MSE pretreatment. Before being shaken with ammonium hydroxide, this particular sample contained 0.95% Cl and 3.20% S; after contact with ammonium hydroxide, the chlorine content was 0.89%, and the sulfur content was 0.33%.

Tensile properties of cellulose formate yarns derived from untreated cotton. — The tensile properties of unmodified cotton yarns treated with various concentrations of thionyl chloride for different reaction-times were determined, and are listed in Table V.

As the reaction time was increased, the breaking strength of the yarns was adversely affected. Tenacities, energy-to-rupture, and elongation-at-break followed a similar trend. The time allowed for preswelling had little effect on retention of strength.

If the reaction time was held constant at 1 h, and the preswelling time was held constant at 5 min, increases in the concentration of the thionyl chloride progressively decreased the strength of the resultant yarns. With 2% thionyl chloride, the strength retention of the yarn was essentially that of untreated cotton (98%), whereas, with 5.5 and 10% thionyl chloride, the strength was lowered to values of 75 and 60%, respectively. At higher concentrations of thionyl chloride, namely, 15 and 20%, the

TABLE V

TENSILE PROPERTIES OF CELLULOSE FORMATE YARNS DERIVED FROM UNTREATED CELLULOSE

Preswelling time in DMF (min)	*Reaction time (min)*[a]	*Thionyl chloride (%)*	*D.s.*[b]	*B.s. (lb)*[c]	*Strength retained (%)*[d]	*Elong. at break (%)*	*Tenacity (g/tex)*	*Energy-to-rupture (in.lb.)*
60	10	5.5	0.19	5.1	98	12.4	14.6	1.9
	60		0.28	3.9	75	11.3	11.0	1.2
	180		0.34	3.2	62	9.8	9.2	0.9
10	60	2	0.12	5.1	98	12.4	15.6	1.8
		5.5	0.21	3.9	75	11.2	11.9	1.3
		10	0.27	3.1	60	9.5	8.8	0.9
		15	0.32	2.7	52	9.9	7.5	0.7
		20	0.38	2.6	50	8.9	7.4	0.7
—[e]	—	—	—	5.2	100	11.7	17.0	2.1

[a] Same conditions as described in Table I, footnote *a*. [b] Calculated by the Eberstadt method, but uncorrected for sulfurous acid ester groups. [c] B.s. = breaking strength. [d] Based on untreated, kiered yarn. [e] Untreated, kiered yarn.

strength was further lessened, but it seemed to become constant at ~50% strength retention for the highest concentration used. Other tensile properties were similarly affected. At a given d.s., the tensile properties appeared to be independent of the concentration of thionyl chloride used in reaching that d.s. Therefore, the effect of concentration of reagent was primarily attributable to its effect on the extent of reaction.

ACKNOWLEDGMENTS

The authors thank Henry Allen and Louise Bosworth of Textile Testing Investigations of our Division for evaluating the tensile properties of the yarns, and Anna Marie Collins for recording the i.r. spectra of the cellulose derivatives.

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