PREPARATION OF FIBROUS CELLULOSE 2,2,2-TRICHLOROACETIMIDATE*

TYRONE L. VIGO AND CLARK M. WELCH

Southern Regional Research Laboratory, Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture, New Orleans, Louisiana 70119 (U. S. A.)

(Received July 31st, 1970; accepted October 7th, 1970)

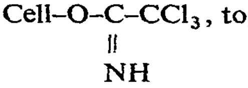
ABSTRACT

Cotton cellulose pretreated with alkali-metal hydroxides reacts with trichloroacetonitrile at room temperature to give cellulose 2,2,2-trichloroacetimidate, a new type of cellulose derivative. Cellulose trichloroacetate is also formed, but this is readily hydrolyzed under mild conditions. Elemental analysis and infrared spectra correlate well with the selective hydrolysis.

Higher degrees of substitution are obtained by using equimolar amounts of cellulose and hydroxide ion, and they increase with increasing concentration of the nitrile. The tensile properties of the modified cellulose, both before and after hydrolysis, are described.

INTRODUCTION

Most investigations of the reaction of cellulose with organic nitriles have been confined to acrylonitrile and similar compounds that undergo Michael addition under alkaline conditions. The only nitriles so employed are chloroacetonitrile and 2- and 3-chloropropionitrile, which react under alkaline conditions to form cellulose ethers[1,2]. Cyanogen chloride is also reported to react with cellulose in basic media[3] to form an imido carbonate ester, but, to date, no simple imido esters of cellulose have been prepared or characterized.

The present paper describes the reaction of trichloroacetonitrile (TCA) with cellulose in strong alkali to yield cellulose 2,2,2-trichloroacetimidate,  $\mathrm{Cell{-}O{-}}\underset{\underset{\displaystyle \mathrm{NH}}{\|}}{\mathrm{C}}\mathrm{{-}CCl_3}$, together with cellulose trichloroacetate. The reactions of this nitrile are unique, in that it readily forms imidates under alkaline conditions as previously described by Cramer *et al.*[4], who studied its addition to simpler alcohols.

The effects, on the degree of substitution (D.S.), of the type of base catalyst and of its concentration are reported, as well as the hydrolytic stability, infrared spectra, and tensile properties of the resulting imidates.

---

[*] Presented at the 160th National Meeting of the American Chemical Society, Chicago, Illinois, September 13–18, 1970.

EXPERIMENTAL

The cellulose was loose-twist, 12/3 (tex-151), Deltapine, cotton yarn purified by kier boiling. Trichloroacetonitrile (Aldrich Chemical Co.**) and carbon tetrachloride were reagent grade; the solutions of alkali-metal hydroxide and acetic acid were prepared from reagent-grade, commercial materials.

Yarns (as 2-g skeins) were immersed slack in an excess of the alkali-metal hydroxide solution for 30 min at room temperature, centrifuged for 3 min at 2850 r.p.m., and then treated on a mechanical shaker with 100 g of trichloroacetonitrile–carbon tetrachloride for 1 h. (All solutions described in the Tables and Figures are on a wt/wt basis.) The yarns described in Table I were then washed by successive immersion in 100 ml of carbon tetrachloride for 5 min, for 5 min in 0.6% (wt/wt) aq. acetic acid (to neutralize alkali remaining in the treated cellulose after centrifugation), and in distilled water for 5 min, centrifuged for 5 min at 2850 r.p.m., and air-dried. The washing procedure for the samples described in Table II differed in that, after being washed in carbon tetrachloride, they were washed in an excess of tap water for 30 min, and allowed to air-dry.

Hydrolysis of the dried yarns was conducted by (*a*) washing in an excess of tap water for 30 min at room temperature, or (*b*) boiling for 30 min in 500 ml of distilled water; subsequently, each yarn was centrifuged for 5 min, and allowed to air-dry.

Elemental analyses for nitrogen were performed by the Kjeldahl method, and for chlorine, by X-ray fluorescence. The values are uncorrected for moisture content. Infrared spectra were recorded on a Perkin–Elmer 137B Infracord spectrophotometer for discs of the cellulose derivative in potassium bromide. Solubilities in cuene (cupriethylenediamine hydroxide) were determined as described by Frick *et al.*[5].

Differential dyeing tests were performed as follows: for every gram of treated cotton, 20 ml of a stock solution containing 0.5% (wt/wt) of Pontamine Fast Blue RRL ("175%")–0.5% of Celliton Fast Yellow RRA–0.5% of Triton X-100 was used, together with distilled water (50 ml). The sample was boiled in this solution for 5 min, and removed; 10% sodium sulfate (5 ml) was added and the mixture was boiled for another 5 min; the yarn was then washed for 20 min with tap water, and air-dried.

The breaking strength and elongation-at-break of the yarns were determined by ASTM method D-2256-64T. Tenacity, energy-to-rupture, toughness, and stiffness were calculated from an automatic integrator attached to an Instron tester**.

RESULTS AND DISCUSSION

The reaction of cotton cellulose yarns with TCA takes place only in the presence of strong alkali, and is not subject to general basic catalysis. Ammonium hydroxide, sodium carbonate, sodium hydrogen carbonate, and such organic amines as pyridine

---

**Mention of a company or product by the U. S. Department of Agriculture does not imply approval or recommendation of the company or product to the exclusion of others that may also be suitable.

TABLE I

EFFECT OF CONCENTRATION OF TRICHLOROACETONITRILE ON THE FORMATION OF CELLULOSE TRICHLOROACETIMIDATE

TCA, %[a]	*Mole ratio Cell-OH/OH^-/TCA*	*Gain in wt. (%)*	*Apparent D.S.*[b]	*N, % Calc.*[b]	*Cl, % Calc.*[b]	*N, % Found*	*Cl, % Found*	*Atomic ratio Cl/N, found*	*Cuene time (min)*[c]	*Diff. dye test*
5	1:0.82:2.78	88.1	0.99	4.54	34.40	1.29	36.40	11.1	B 10	yellow
10	1:0.89:5.63	153.0	1.74	5.90	44.70	2.98	50.02	6.6	I 10	intense yellow
15	1:0.88:8.44	200.0	2.25	6.45	49.20	3.59	45.36	5.0	I 10	intense yellow

[a] All yarns were immersed in 20% (wt/wt) aq. potassium hydroxide, centrifuged for 3 min, allowed to react with the respective TCA solution for 1 h, immersed in dilute acetic acid to neutralize the alkali, washed briefly with tap water, centrifuged for 5 min, and air-dried. [b] Calculated from gains in weight, assuming that imidate only was present. [c] B = ballooned; I = insoluble.

TABLE II

EFFECT OF CONCENTRATION OF HYDROXIDE ION ON FORMATION OF CELLULOSE TRICHLOROACETIMIDATE

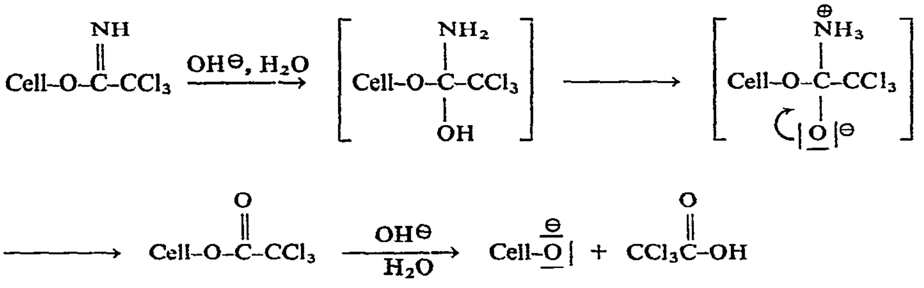
Concentration (g/100 g) of potassium hydroxide used in pretreatment[a]	*Mole ratio of Cell-OH/OH^-/TCA*	*Gain in wt. (%)*	*Apparent D. S.*[b]	*N, % Calc.*[b]	*Cl, % Calc.*[b]	*N, % Found*	*Cl, % Found*	*Atomic ratio Cl/N, found*	*Cuene time (min)*[c]	*Diff. dye test*
5	1:0.05:3.12	18.9	0.22	1.53	12.00	0.68	8.78	5.1	D 1	light blue
10	1:0.16:2.91	31.1	0.35	2.34	17.40	1.29	16.48	5.1	D 10	yellow-blue
20	1:0.86:2.79	123.4	1.39	5.36	40.70	1.62	27.02	6.6	I 10	yellow
32	1:1.63:2.77	10.3	0.13	0.94	7.50	0.40	3.57	3.5	D 2	blue

[a] Yarns were centrifuged for 3 min after immersion in alkali, and then allowed to react with 5% TCA–95% CCl_4 for 1 h at 25°, washed with tap water for 30 min, and air-dried. [b] Calculated from gains in weight, assuming that imidate only is present. [c] D = dissolved; I = insoluble.

or triethylenediamine in basic pretreatments or as catalysts were ineffective in causing reaction of cellulose with the nitrile.

Of the solvents used for the reaction (chloroform, acetone, ethanol, and carbon tetrachloride), carbon tetrachloride gave the highest D.S. with a particular alkaline pretreatment, and was used as the solvent for all subsequent reactions. Although aqueous solutions of lithium, sodium, or potassium hydroxide were satisfactory for alkaline pretreatments of the cellulose, the gains in weight and D.S. were markedly dependent on the concentration of the particular alkali-metal hydroxide used and on the molar ratio of hydroxide ion to cellulose.

Potassium hydroxide for preteatment was studied in detail, and the results are given in Table II. As the concentration of the hydroxide is increased from 5 to 10%, the D.S. correspondingly increases from 0.22 to 0.35 substituent groups per D-glucose residue; when the concentration is raised to 20%, the D.S. increases to a value of 1.39. However, with concentrations greater than 20%, the D.S. falls off drastically, and is even less than that obtained by pretreatment with 5% potassium hydroxide. The maximum gains in weight are achieved when the molar ratio of hydroxide ion to cellulose approaches unity. If the ratio exceeds unity, the cellulose trichloroacetimidate is hydrolyzed to cellulose, apparently by the following mechanism.



The formation of cellulose trichloroacetate as a hydrolysis intermediate is suggested by the high Cl:N ratio observed for most of the samples described in Table II. The patent literature describes a similar transformation of polymeric imidate hydrochlorides into polyesters by hydrolysis under neutral conditions[6].

For cellulose trichloroacetimidate, the Cl:N molar ratio should be 3 to 1. However, the ratio observed is much greater, particularly in samples having high weight-gains. The formation of cellulose trichloroacetate by the foregoing mechanism would result in lessening of the nitrogen content, and yet the chlorine content would stay relatively high. When an excess of base is added, as with 32% potassium hydroxide, the trichloroacetate group is probably hydrolyzed as fast as the compound is formed, and, therefore, the ratio is relatively close to that calculated for a trichloroacetimidate group alone. This mechanism also accounts for the variability of weight-gains observed on using 20% potassium hydroxide for alkaline pretreatment; experiments described in Tables III and IV utilized neutralization of the excess of base with dilute acetic acid, in order to minimize the variability caused by formation of both cellulose trichloroacetimidate and cellulose trichloroacetate.

The ability of cellulose imidates to dissolve readily in such cellulose solvents as cuene decreases with increasing D.S., and is probably indicative of a blocking action by the large functional groups rather than an indication of crosslinking (see Table II). The ability of the modified cellulose to adsorb disperse acetate dyes in preference to direct dyes also increases with increasing D.S., as noted in Table II.

The effect of increasing the concentration of the TCA at a fixed concentration of alkali is shown in Table I. The apparent D.S. increases from 0.99 to 2.25 with increasing concentration of TCA. As expected, the Cl:N ratios are much higher than calculated for the imidate derivative alone, but they decrease with increasing TCA concentration. All of the samples showed moderate to marked diminution of solubility in cuene, and were receptive to acetate dyes.

The i.r. spectra of native cellulose (Curve A) and of these derivatives (Curves B–D) are shown in Fig. 1. The first region of interest is that of 5.5–6.1 μm. The C=NH stretch is very intense and occurs[7] at 6.0 μm. A shoulder is also noted at 5.7–5.8 μm, and is probably due to the carbonyl stretch of cellulose trichloroacetate. The second region of interest is 12.0–13.5 μm. The absorptions observed at 12.0 and 12.8 μm

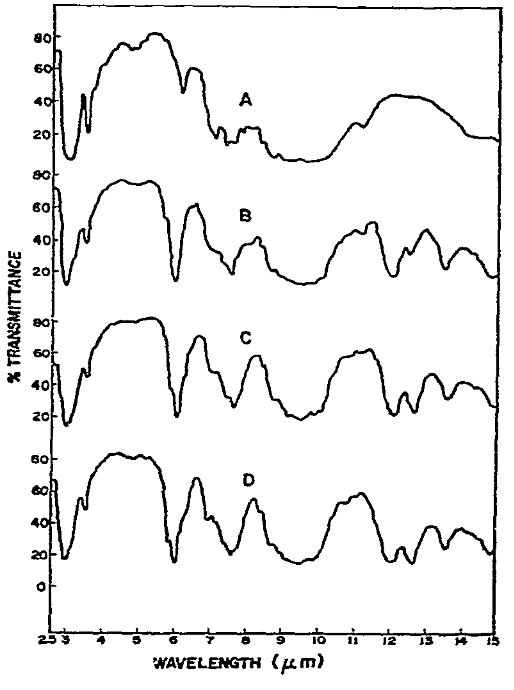


Fig. 1. Infrared spectrum of 12/3 kiered, cotton yarns treated with (A) no reagents; (B) 20% potassium hydroxide, and then 5% TCA–95% CCl$_4$; (C) 20% potassium hydroxide, and then 10% TCA–90% CCl$_4$; and (D) 20% potassium hydroxide, and then 15% TCA–85% CCl$_4$.

are attributed to the C–Cl stretch of the cellulose trichloroacetimidate, and that at 13.5 μm to the C–Cl stretch of cellulose trichloroacetate[7].

Hydrolysis of these three samples (described in Table III) at room temperature produces differences in their infrared spectra consistent with preferential hydrolysis of trichloroacetate groups; curves A–C in Fig. 2 depict these differences. Even after hydrolysis, the cellulose treated with 5% TCA exhibits a strong carbonyl absorption, as well as the imino stretch absorption (Curve A). However, yarns treated with 10 or 15% TCA, and then hydrolyzed at 25°, show little or no carbonyl absorption (Curves B and C); they also show differences in the region of 12–13.5 μm. Unhydrolyzed samples (Fig. 1, Curves B, C, and D) have three absorptions in this region, whereas hydrolyzed samples pretreated with 10 or 15% TCA (Fig. 2, curves B and C) show only two, namely those at 12.0 and 12.8 μm, with some shift of the absorption at 12.0 μm. The sample treated with 5% TCA (hydrolyzed) still showed some absorption at 13.5 μm (Fig. 2, Curve A). The disappearance of the peak at 13.5 μm may be due to the removal of the trichloroacetate group, since this absorption is apparently due to the C–Cl stretch of this moiety.

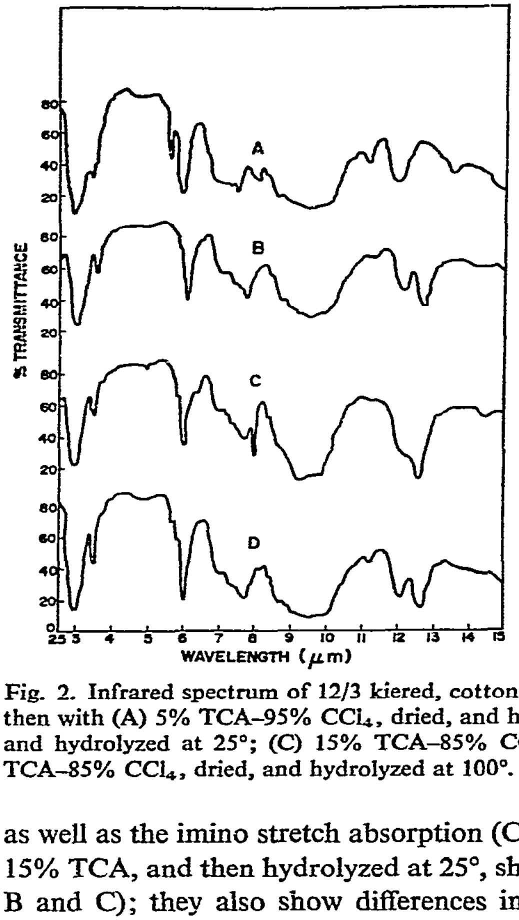


Fig. 2. Infrared spectrum of 12/3 kiered, cotton yarns treated with 20% potassium hydroxide, and then with (A) 5% TCA–95% CCl_4, dried, and hydrolyzed at 25°; (B) 10% TCA–90% CCl_4, dried, and hydrolyzed at 25°; (C) 15% TCA–85% CCl_4, dried, and hydrolyzed at 25°; and (D) 15% TCA–85% CCl_4, dried, and hydrolyzed at 100°.

Elemental analyses, particularly the Cl:N ratio and the values for percent N, of these hydrolyzed samples are consistent with the i.r. spectra observed. The carbonyl

TABLE III

HYDROLYTIC STABILITY OF CELLULOSE TRICHLOROACETIMIDATE YARNS

Temp. of hydrolysis[a] *(degrees)*	*Gain in weight*		*Apparent D.S. after hydrolysis*[b]	*N, % Calc.*[b]	*Cl, % Calc.*[b]	*N, % Found*	*Cl, % Found*	*Atomic ratio Cl/N, found*	*Cuene time*[c] *(min)*	*Diff. dye test*
	Original[b] *(%)*	*Final (%)*								
25	86.6	31.5	0.36	2.33	17.70	1.33	20.30	6.0	B 10	yellow-blue
25	162.3	69.3	0.79	4.03	30.40	3.74	45.07	4.8	I 10	intense yellow
25	210.1	101.5	1.15	4.90	37.00	4.48	42.44	3.8	I 10	intense yellow
100	88.1	20.8	0.24	1.65	12.80	0.92	15.10	6.5	B, D 10	blue-yellow
100	153.0	48.0	0.55	3.22	24.40	3.04	30.01	3.9	B 10	intense yellow
100	200.0	60.3	0.69	3.70	28.00	3.49	37.59	4.3	B 10	intense yellow

---

[a] Hydrolysis time, 30 min; after treatment with water, all yarns were centrifuged for 5 min and then air-dried. [b] Samples to be hydrolyzed at 25° were prepared as duplicates of samples hydrolyzed at 100° (see Table I for preparation). [c] B = ballooned; D = dissolved; I = insoluble.

TABLE IV

TENSILE PROPERTIES OF CELLULOSE TRICHLOROACETIMIDATE YARNS BEFORE AND AFTER HYDROLYSIS

Conc. of TCA (%)	*Temp. of hydrolysis* (*degrees*)	*Apparent D.S.*	*B.S.*[a]	*Elong. at break* (%)	*Energy-to-rupture* (*lb*)	*Tenacity* (*g/tex*)	*Toughness*	*Stiffness*
5	—	0.99[b]	6.4	26.3	4.8	8.9	0.66	33.8
5	25	0.36	6.2	21.8	4.1	12.6	0.84	57.7
5	100	0.24	6.2	23.9	4.0	13.3	0.85	55.6
10	—	1.74[b]	5.7	39.9	6.6	5.3	0.62	13.3
10	25	0.79	6.5	39.3	6.7	8.1	0.85	20.6
10	100	0.55	6.5	38.3	6.2	9.1	0.86	23.7
15	—	2.25[b]	5.6	56.8	10.9	3.3	0.64	5.8
15	25	1.15	5.1	49.4	7.8	4.4	0.67	8.9
15	100	0.69	5.5	52.0	8.0	5.8	0.85	11.1
		none[c]	6.6	23.6	4.2	17.9	1.15	75.8
		none[d]	5.3	10.5	1.9	17.6	0.63	167.0

[a] B.S. = breaking strength in lb. [b] Same samples as in Table I; all others are described in Table III. [c] Immersed in 20% potassium hydroxide, and then washed with tap water and air-dried. [d] Untreated, kiered yarn.

intensity decreases concomitantly with the Cl:N ratio; the percent N value is in good agreement with the values calculated for cellulose trichloroacetimidate (see Table III). Hydrolysis with hot water also produces the same trend, although the i.r. spectrum of the sample treated with 15% TCA shows three absorptions in the region of 5.5–6.1 μm. It is possible that this new absorption at 5.5 μm is due to an imido stretch at a secondary hydroxyl group at C-2 or C-3 of the D-glucose residues, which would have an environment different from that of the substituent at the primary hydroxyl group. The solubility in cuene decreases and the receptivity to acetate dyes increases as the D.S. or weight-gain increases.

The tensile properties of these derivatives, both before and after selective hydrolysis, are shown in Table IV. A treatment with 5% TCA causes little change in breaking strength or elongation compared to that caused by a pretreatment with 20% potassium hydroxide alone, but causes some lessening of the tenacity and toughness. With 10 or 15% TCA, breaking strengths are slightly lowered, but elongation values are greatly increased, and remain very high (39–57%), even after hydrolysis; the tenacities are lessened, but hydrolysis of the trichloroacetate group increases them somewhat. For all of the products, the stiffness of the derivatives is much lower than that of native cellulose, and it decreases as the degree of substitution increases.

ACKNOWLEDGMENTS

The authors acknowledge the contributions of Lawrence Brown and Biagio Piccolo in performing the elemental analyses, and Henry Allen in determining the tensile properties of the yarns. We especially thank Anna Marie Collins for the preparation of some of the samples and recording of their i.r. spectra.

REFERENCES

1 H. Dreyfus, U. S. Pat. 2,015,104 (1935); *Chem. Abstr.*, 29 (1935) 7657.
2 H. Dreyfus, U. S. Pat. 2,233,475 (1941); *Chem. Abstr.*, 35 (1941) 3814.
3 R. Haller and A. Heckendorn, U. S. Pat. 1,895,544 (1933); *Chem. Abstr.*, 27 (1933) 2577.
4 F. Cramer, K. Pawelzik, and H. J. Baldauf, *Chem. Ber.*, 91 (1958) 1049.
5 J. G. Frick, Jr., L. C. Weiss, B. A. K. Andrews, A. T. Moore, A. B. Cooper, R. T. O'Connor, A. G. Pierce, W. A. Reeves, and M. L. Rollins, *Amer. Dyestuff Reptr.*, 52 (1963) P952.
6 D. D. Coffman and F. C. McGrew, U. S. Pat. 2,317,155 (1943); *Chem. Abstr.*, 37 (1943) 5735.
7 L. N. Bellamy, *The Infra-red Spectra of Complex Molecules*, 2nd ed., Wiley, New York, 1960, pp. 179 and 263.