

## ***Thermal Behavior of Cellulose Imidates: Cellulose Trichloroacetimidate\****

### **INTRODUCTION**

Until recently, the thermal behavior of cellulose derivatives has received scant attention in the literature. Hobart and Mack<sup>1,2</sup> have investigated the thermal dissociation of various cellulose carbamates by the use of DTA, TGA, and DSC (differential scanning calorimetry), while Buntyakov et al.<sup>3</sup> and Patel et al.<sup>4</sup> have described the thermal stability of cellulose acetate by DTA and TGA.

Previous work in these laboratories<sup>5</sup> has shown that the reaction of trichloroacetonitrile (TCA) with cotton cellulose in the presence of alkali metal hydroxides yields cellulose trichloroacetimidate as well as the by-product cellulose trichloroacetate, indicated by elemental analyses and infrared spectra. It was suggested that selective cold or hot water hydrolysis removed the more labile trichloroacetate moiety, since the Cl/N ratio and the infrared spectra were in good agreement for cellulose trichloroacetimidate.

The present investigation deals with the thermal stability of cellulose trichloroacetimidate-cellulose trichloroacetate, both before and after hot water hydrolysis. The data obtained from DTA and TGA (dynamic and isothermal) are described and discussed in relation to the hydrolytic stability of the trichloroacetate group. Kinetic data have been calculated from the curves, and explanations for the observed transitions and their relationship to imidate hydrolysis are discussed.

### **EXPERIMENTAL**

The cellulose was loose-twist 12/3 Deltapine kiered cotton yarn. Trichloroacetonitrile (Aldrich Chemical Co.) and carbon tetrachloride were reagent grade; potassium hydroxide and acetic acid solutions were made from reagent-grade materials.

The yarns were immersed slack as 2-g skeins in excess 20% aqueous potassium hydroxide at 25°C for 30 min, centrifuged for 3 min at 2850 rpm, then shaken 1 hr in 100 g of 5% to 15% TGA in carbon tetrachloride. The yarns were then washed for 5-min intervals with (a) carbon tetrachloride (100 ml), (b) 0.6% aqueous acetic acid sufficient to neutralize excess alkali, (c) distilled water (100 ml), and then centrifuged 5 min at 2850 rpm and air dried. Hydrolysis of the dried yarns was carried out by boiling in 500 ml distilled water for 30 min, centrifuging 5 min, and air drying.

Some elemental analyses were performed by a commercial laboratory, while others were performed in our laboratories (nitrogen by Kjeldahl and chlorine by x-ray fluorescence). The values are uncorrected for moisture content in the cellulose.

The samples were prepared for use in the differential thermal analyzer, duPont Model 900, by the method of Hobart and Mack.<sup>1,2</sup> The following operational parameters were used: program rate, 25°/min; *T* scale, 1°C/min, and an atmosphere of purified dry nitrogen at 2 standard ft<sup>3</sup>/hr.

Dynamic thermogravimetric analysis was performed on the duPont 950 TGA apparatus by cutting the yarn into several pieces and centering on the tared pan. The following operation parameters were used: heating rate, 5°C/min, and a vacuum atmosphere of 100–150 microns. Isothermal thermogravimetric analysis was done on the same instrument by the time base method of Hobart and Mack.<sup>1,2</sup>

The isothermal TGA data were treated by previously published methods.<sup>1,2</sup> After employing a correction factor for the slight decomposition of cellulose, the fraction of substituent remaining at various time intervals was calculated; these results were plot-

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

ted as the logarithm of the fraction remaining versus time. A linear plot for the thermal decomposition signifies a first-order dissociation.

## RESULTS AND DISCUSSION

### Differential Thermal Analysis

DTA was used to investigate the thermal behavior of native cotton, and of cotton treated with 5% and 15% TCA before and after hot-water hydrolysis. A comparison of the DTA curves obtained with that of native cotton and of the unhydrolyzed and hydrolyzed TCA-treated cottons is shown in Figures 1 and 2, respectively.

Cotton treated with 15% TCA and subsequently protected from moisture (Fig. 1, curve C) exhibits a strong endotherm at 145°C and two strong exotherms at 246° and 250°C. The endotherm is not associated with the loss of moisture from the sample since the peak temperature (145°C) is 23° higher than that normally associated with loss of water from cellulose and since an identical curve was obtained on a predried sample. One or both of the exotherms at 246° and 250°C must be associated with the cellulose decomposition since no other thermal changes were observed up to 450°C. The same sample which had been subjected to hot-water hydrolysis (Fig. 2, curve C) exhibited no significant thermal change at 145°C. At higher temperatures, a broad endotherm peaking at 235°C was observed, and at 250°C, a sharp exothermic spike appeared to be superimposed on the endotherm. A comparison of the atomic Cl/N ratios of these samples showed a value of 5.0 for the sample before hydrolysis and a value of 4.3 after hot-water hydrolysis (value should approach 3.0 for cellulose trichloroacetimidate). In addition, the hydrolysis step removed only chlorine (decrease of 45.5% to 37.5%) while the nitrogen content remained essentially constant (3.59% and 3.49%, respectively). These observations are consistent with the low-temperature endotherm (145°C) being associated with the loss of the trichloroacetate group and with the higher temperature transitions resulting from thermal cleavage of the trichloroacetimidate group as well as complex disintegration of the cellulose itself.

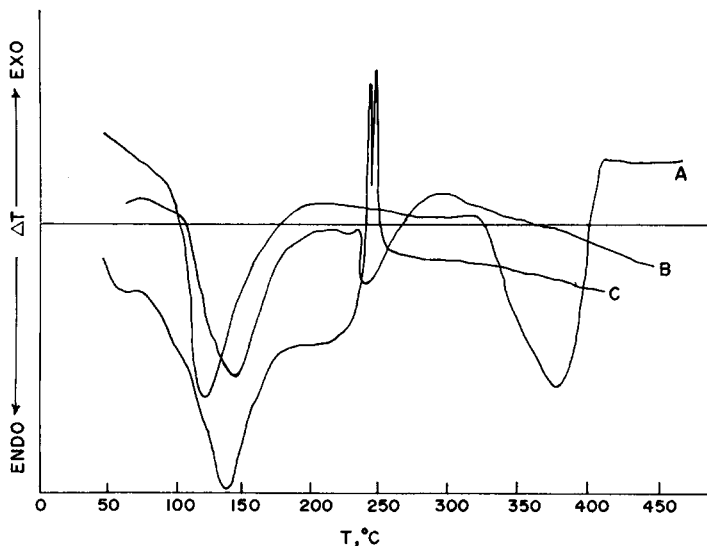


Fig. 1. DTA curves for (A) native cotton, (B) cotton treated with 5% TCA before hydrolysis, (C) cotton treated with 15% TCA before hydrolysis.

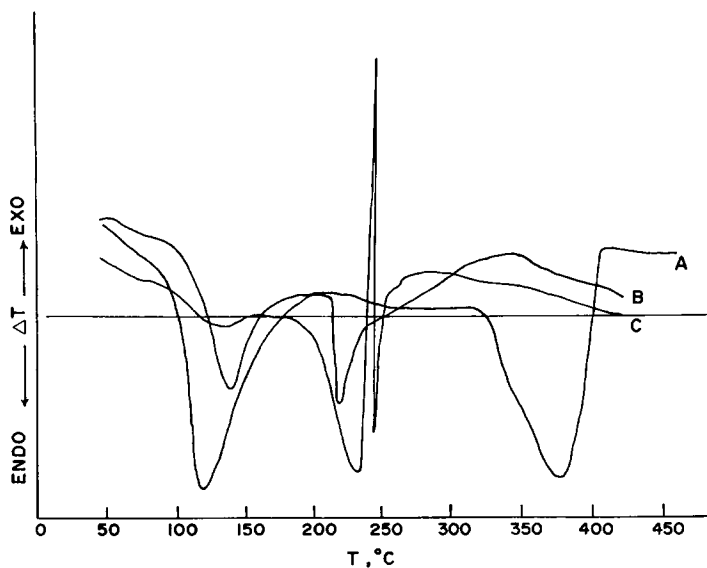


Fig. 2. DTA curves for (A) native cotton, (B) cotton treated with 5% TCA, then hydrolyzed at 100°C, (C) cotton treated with 15% TCA, then hydrolyzed at 100°C.

The correlation between preferential pyrolysis of the trichloroacetate group and hydrolysis of the same species is also observed in the cotton samples treated with lower concentrations of TCA (5%). Comparison of curves B in Figures 1 and 2 (before and after hot water hydrolysis, respectively) showed that in the 145°C region, a considerable decrease in the endotherm was observed as a result of the hydrolysis. In the higher temperature range, there was a moderate change in the endothermic peak temperatures (from 145° to 216°C) and a slight change in peak area. In contrast to the cotton treated with 15% TCA, no exotherms were observed in the region of 245°–250°C, indicating that at lower D.S., the sample behaved more like untreated cotton in that it did not decompose at lower temperatures. The Cl/N ratio also decreased (from 11.1 to 6.5) as a result of the hydrolysis, but failed to approach that for cellulose trichloroacetimidate itself. From these observations and from the elemental analyses (%Cl = 36.40 and %N = 1.29 before, and %Cl = 15.10 and %N = 0.92 after hot-water hydrolysis), it was concluded that only partial hydrolysis of cellulose trichloroacetate was accomplished.

#### Dynamic Thermogravimetric Analysis

To obtain further information on the thermal behavior of the cellulose modified with trichloroacetonitrile (TCA), the same samples described above were also examined via dynamic TGA. The thermal behavior before and after hot-water hydrolysis is shown in Figures 3 and 4.

Native cotton (Figs. 3 and 4, curve A) showed little, if any, weight loss until 350°C, and then underwent rapid decomposition with a residue of 10.5% remaining by the time the temperature approached 400°C. The unhydrolyzed sample of cotton treated with 15% TCA shows two definite stepwise weight losses, one in the region of 140°–150°C and another in the region of 245°–255°C (see Fig. 3, curve C). The initial weight loss by 150°C is 22% followed by a gradual weight loss up to 245°C, then a rapid weight loss in the region of 245°–255°C (55%). This correlates with the endotherms observed in the DTA at 137°C (Fig. 1, curve C) and the intense exotherms at 246° and 250°C. However, when this sample is hydrolyzed with hot water, its TGA pattern is significantly

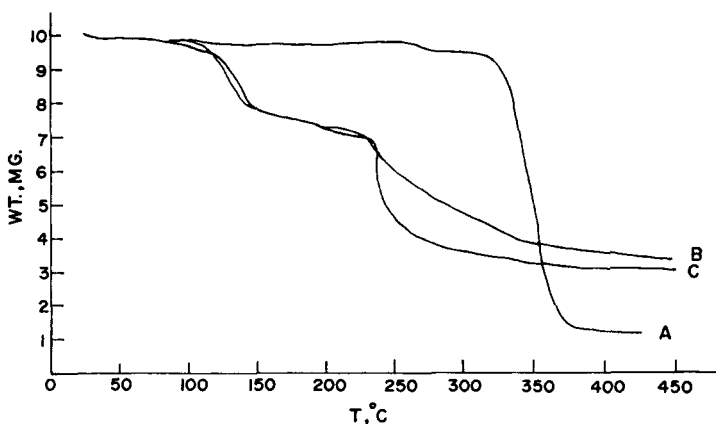


Fig. 3. Dynamic TGA curves for (A) native cotton, (B) cotton treated with 5% TCA before hydrolysis, (C) cotton treated with 15% TCA before hydrolysis.

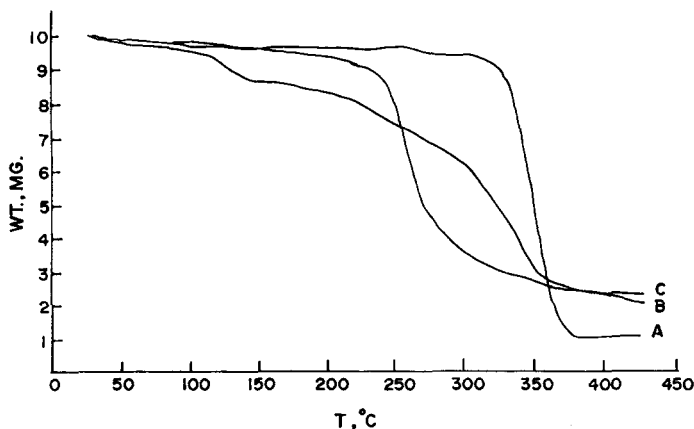


Fig. 4. Dynamic TGA curves for (A) native cotton, (B) cotton treated with 5% TCA, then hydrolyzed at 100°C, (C) cotton treated with 15% TCA, then hydrolyzed at 100°C.

altered (Fig. 4, curve C). It loses only 4% of its weight by 150°C, then undergoes a dramatic weight loss starting at 245°C. Comparison with its DTA curve (Fig. 2, curve C) shows only a small (negligible) endotherm at 135°C, an intense endotherm at 235°C, followed by a very intense exothermic spike superimposed upon it at 250°C. The apparently greater loss of weight in the temperature range of 235°–285°C for the hydrolyzed sample (relative to the unhydrolyzed sample) seems to indicate increased ease of cellulose decomposition in the presence of trichloroacetimidate groups. In unhydrolyzed samples the induced decomposition of cellulose is preceded and masked by cellulose trichloroacetate decomposition. The observations are consistent with the low temperature (150°C) loss of trichloroacetate and complex decomposition of cellulose and cellulose trichloroacetimidate at higher temperatures (235°–250°C). Samples of cotton treated with 5% TCA (unhydrolyzed) (see Fig. 3, curve B) lose 22% of their total weight by 150°C, then undergo another weight loss in the vicinity of 250°C, and have a residue of 35% by 400°C. These weight losses also correlate with the DTA (Fig. 1, curve B),

showing that there is a loss of chemical moiety at these temperatures. The curve for the hydrolyzed sample (Fig. 4, curve B) shows that the initial weight loss up to 150°C is only 13.5% and that further weight loss is gradual. The thermogravimetric behavior is again in agreement with the DTA (Fig. 2, curve B), and the final residue of the sample is 22% by 400°C; however, the cotton treated with the 5% TCA, on hydrolysis, does not lose all of the trichloroacetate group, since it still loses some weight in the region of 150°C (ca. 13.5%).

The agreement in the weight losses observed in the TGA and transitions exhibited in the DTA at the same temperatures provided additional information and evidence that this was due to thermally labile groups on the modified cellulose. The appearance of endotherms and exotherms can therefore not be attributed to other phenomena such as phase transitions.

#### Isothermal Thermogravimetric Analysis

Since the sample of cotton treated with 5% TCA did not lose all of the trichloroacetate group on hydrolysis, only the sample treated with 15% TCA (unhydrolyzed) was subjected to isothermal TGA. Runs were made on this sample at four different temperatures: 97°, 107°, 114°, and 127°C, on the time base scale. The samples were dried to constant weight (30 min at 75°C under high vacuum) before the run was started to ensure removal of all traces of moisture. The curves obtained for each of the four runs are shown in Figure 5, and the semilogarithmic plot of the data obtained from these

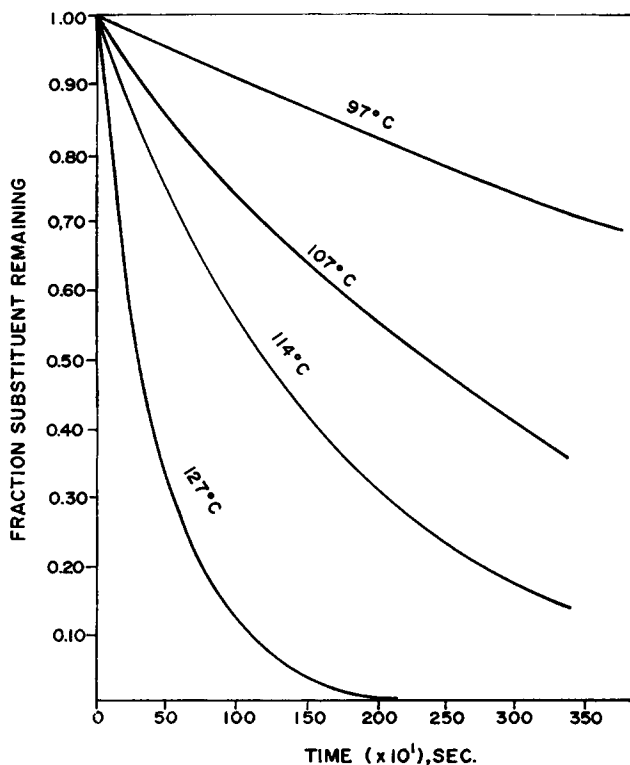


Fig. 5. Plot of fraction of substituent remaining vs. time for the isothermal decomposition of cotton treated with 15% TCA before hydrolysis.

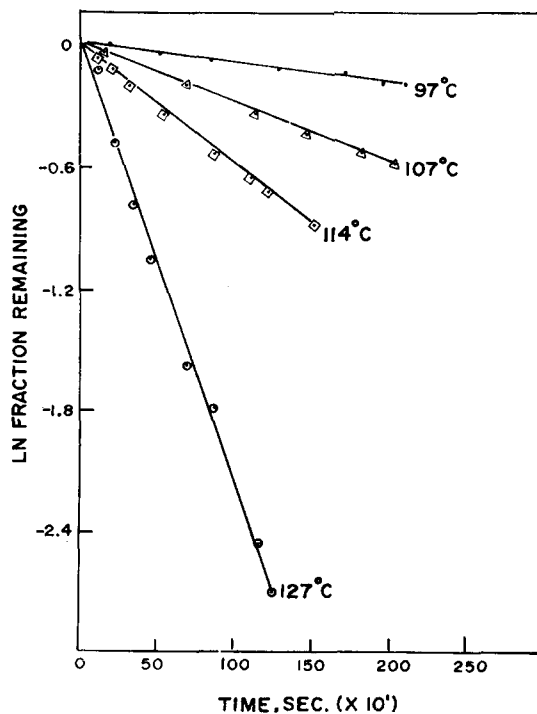


Fig. 6. Plot of  $\ln$  fraction remaining vs. time at various temperatures for the decomposition of cotton treated with 15% TCA before hydrolysis.

curves of fraction of substituent remaining (using total substituent as 30% by weight of the sample) versus time is shown in Figure 6. A small correction factor was used to compensate for the weight loss observed for cellulose itself at these temperatures and sensitivity settings. The results show that the rate of weight loss follows first-order kinetics because the points fall on a straight line from which the rate constants were obtained by a least-squares treatment. A plot of the rate constants at the four temperatures versus the reciprocal of the absolute temperature also gave a straight line from which enthalpy and entropy values were calculated. These results are listed in Table I and plotted in Figure 7.

TABLE I  
Calculation of Thermodynamic Parameters From the Isothermal  
Decomposition of Cotton Treated with 15% TCA (Before Hydrolysis)<sup>a</sup>

Temp., °C	Temp., °K	$k$ (rate)	$\log k$	$1/T$
97	370	$-9.45 \times 10^{-5}$	-4.025	$2.70 \times 10^{-3}$
107	380	$-2.96 \times 10^{-4}$	-3.529	$2.63 \times 10^{-3}$
114	387	$-5.72 \times 10^{-4}$	-3.243	$2.58 \times 10^{-3}$
127	400	$-21.4 \times 10^{-4}$	-2.670	$2.50 \times 10^{-3}$

<sup>a</sup>  $\Delta H_{\text{act}}$ /mole was calculated to be 30.89 kcal;  $\Delta S_{\text{act}}$ /mole was calculated to be +0.0034 eu.

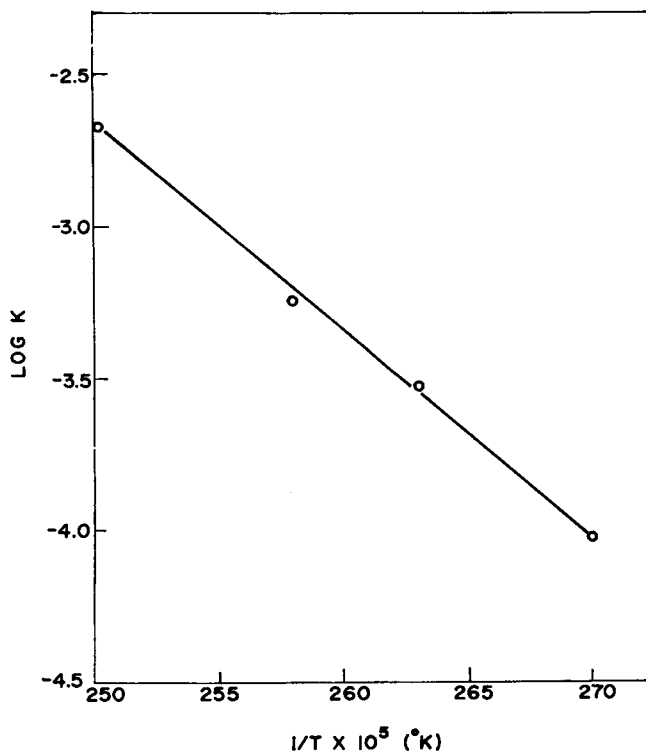
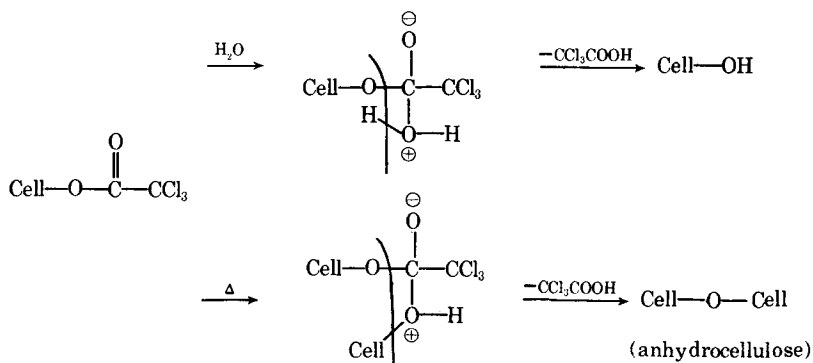


Fig. 7. Plot of  $\log k$  vs.  $1/T \times 10^5$  for the decomposition of cotton treated with 15% TCA before hydrolysis.

**Mechanism of Thermal Decomposition**

The similarity between the facile hydrolysis and pyrolysis of cotton treated with TCA (unhydrolyzed) is seen in the following suggested scheme:



The upper scheme is the generally accepted mechanism for the uncatalyzed hydrolysis of esters with electron-withdrawing groups on the acyl carbon atom. The lower scheme is one possible mechanism for the thermal dissociation of the ester via alcoholysis with a neighboring cellulosic group on the same glucose unit or on a parallel chain to produce

the "anhydrocellulose" by loss of trichloroacetic acid. This type of structure has been proposed as the result of the alkaline dissociation of tosyl esters of cellulose.<sup>6</sup> The transition state is most likely acyclic in view of the slightly positive entropy values observed. Olefinic celluloses may also be a product of the pyrolysis.

The results obtained from the dynamic DTA and TGA, the change in the atomic Cl/N ratio after hydrolysis coupled with the corresponding thermal changes, and the kinetic data calculated from the isothermal TGA results in Table I are consistent with the above mechanism. The insolubility in cuene of the modified cotton (15% TCA-unhydrolyzed) after being heated to 150° and 275°C (loss of trichloroacetate and trichloroacetimidate groups, respectively) is also consistent with this mechanism.

Dissociations similar to those postulated are generally first order and endothermic; therefore, the entropy of activation would be negligible since no strained or rigid configuration of the intermediate would occur. At higher temperatures, thermal dissociations are complex in that degradation of the cellulose itself occurs simultaneously with the dissociation of the trichloroacetimidate. The DTA curves substantiate this conclusion. Unhydrolyzed cotton (15% TCA treatment) shows an exothermic spike superimposed on a large and broad endotherm; this is indicative that at least two, and probably more, dissociations are superimposed upon one another. In the same temperature range, the TGA exhibits only a smooth weight loss, indicative of a single reaction. In addition, the amount of residue or char that remains is much higher than normally encountered with native cotton, suggesting that the trichloroacetimidate dissociation alters the dissociation of the cellulose.

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The authors wish to acknowledge Lawrence E. Brown and Biagio Piccolo for the determination of some of the elemental analyses. We wish to especially acknowledge Stanley R. Hobart for helpful discussions in running the computer program and determination of the reaction kinetics.

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Received January 20, 1971

Revised April 23, 1971