

Cellulose Propionylpropionate as a Side Product in the Reaction of Cotton Cellulose with Propionyl Chloride

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Synopsis

In the reaction of cotton cellulose fiber with propionyl chloride in pyridine-DMF medium, the degree of substitution based on weight gain was much higher than that based on saponification. Gas-liquid chromatograms of the pyrolysis products of the samples showed an extra peak. This was identified as 3-pentanone, which arises from the pyrolysis of α -propionylpropionic acid, a substance which was proposed by Malm and co-workers as a possible side product. This conclusion was further confirmed by the infrared and NMR spectra of the liquid, collected fractionally on pyrolysis of the sample. Quantitative GLC showed that one out of every four hydroxyl groups is substituted with an α -propionylpropionyl moiety, the rest with propionyl groups. A possible mechanism for the side reaction has been proposed.

INTRODUCTION

In the course of our studies on the cellulose propionates, a peculiarity was observed in the reaction of cellulose with propionyl chloride in dimethylformamide (DMF) and pyridine. It was noted that the degree of substitution (DS), based on weight gain, far exceeded that by saponification. The work reported here describes how this apparent anomaly was solved by identification and estimation of the extra component (α -propionylpropionate) that arises from a side reaction.

EXPERIMENTAL

Chemicals

Propionyl chloride and dimethylformamide were Eastman reagent grade and were used as received. Pyridine and methanol were Baker analyzed reagent grade. The 3-pentanone was practical grade, supplied by Matheson, Coleman, and Bell. It gave only one peak in the gas-liquid chromatogram and was considered to be of sufficient purity to be used without further purification.

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Preparation of the Sample

The samples were prepared by the acid chloride-pyridine method¹ in a laboratory reactor as described by Stanonis et al.² The molar quantity of propionyl chloride was four times the estimated total hydroxyl groups of the sample of cellulose taken (7/2 cotton yarn). The volume of pyridine was double that of the propionyl chloride and was diluted with an equal volume of DMF.

For two samples, 11 and 12, a mixture of propionic anhydride and propionyl chloride was used as the propionylating reagent, the ratio of the anhydride to the chloride being such that two-thirds of the propionyl groups could come from the anhydride and one-third from the chloride, the ratio of total cellulosic hydroxyl to propionyl being maintained at 1:4. Other conditions were maintained constant in both series.

The required amount of propionyl chloride was added dropwise into the measured quantity of a mixture of pyridine and DMF at 5–10°C. and the solution, preheated to 75°C., was added to the dried sample of cellulose contained in a vessel also preheated to the bath temperature. The reaction was carried out in a thermostatted bath at $75 \pm 2^\circ\text{C}$. for different periods of time according to the degree of substitution desired.

Chromatography

An F & M Model 500 gas-liquid chromatograph with disk integrator was used in the chromatographic experiments.

In experiments relating integrated area to the amount of 3-pentanone, the latter was diluted to five times its volume with acetone, and different known quantities were injected into the chromatograph with a microsyringe.

In order to detect nonuniformity of reaction in the treated yarn, 2-mg. specimens from different parts of the same lot were weighed and sealed into glass capillaries. Each ampule was then introduced into the injection port of the chromatograph, kept at the injection port temperature of 375°C., for 7 min., and then broken. It was found that the integrated areas of the appropriate peak for the same sample varied within reasonable limits. Also, the integrated areas followed per cent propionyl, calculated from the weight increase, in a linear relationship, showing that the increase of weight is closely related to the ester group combined with the cellulose.

All the quantitative experiments were done with the same column with the use of silicone gum rubber adsorbed on Chromosorb W, and other conditions were kept constant as far as practicable.

Infrared Spectra

A Perkin-Elmer Model 21 double-beam spectrophotometer was used to obtain the infrared spectra.

Nuclear Magnetic Resonance Spectra

A Varian A-60A NMR spectrometer was used to obtain the spectra; tetramethylsilane was used as reference.

Degree of Substitution

Degree of substitution was measured both by weight gain and by the saponification method described by Genung and Mallatt.³ The results of varying the time of saponification showed that at least 48 hr. is necessary for complete saponification.

RESULTS AND DISCUSSION

Facts Indicating Side Reaction

Table I shows the degree of substitution (DS) of the various samples as estimated by saponification and by weight-gain methods. It is seen that the DS as determined by weight gain is always higher than that by saponification. In the case of the two highest substitutions it exceeds the theoretical value of 3.0, being in one case as high as 4.2. However, DS as determined from weight gain followed a linear relationship with that determined by saponification, the latter being always within the theoretical maximum (Fig. 1). This suggests that some other compound, contributing to the weight gain but not to the saponification value, is being produced in a side reaction; or acyl groups occurring in a constant proportion have different weights. The carbon-hydrogen analysis of the samples did not

TABLE I
Contribution of Propionate and Propionylpropionate to DS

Sample no.	Degree of substitution		Propionic acid by GLC, %	Degree of substitution		
	Weight gain	Saponification		As propionate (determined)	As α -propionylpropionate	
					(calculated)	Total DS (calculated)
1	0.33	0.24	3.90	0.13	0.10	0.23
2	0.63	0.37	7.44	0.28	0.17	0.45
3	0.73	0.44	11.91	0.45	0.14	0.59
4	1.12	0.75	13.40	0.56	0.28	0.84
5	1.35	1.01	19.36	0.84	0.25	1.09
6	1.71	1.37	18.86	0.94	0.38	1.32
7	2.52	1.72	26.70	1.46	0.53	1.99
8	2.88	2.00	27.55	1.68	0.60	2.28
9	3.40	2.34	30.28	2.01	0.69	2.70
10	4.27	2.94	32.60	2.37	0.75	3.12
11	0.70	0.69	—	—	—	—
12	0.90	0.85	—	—	—	—

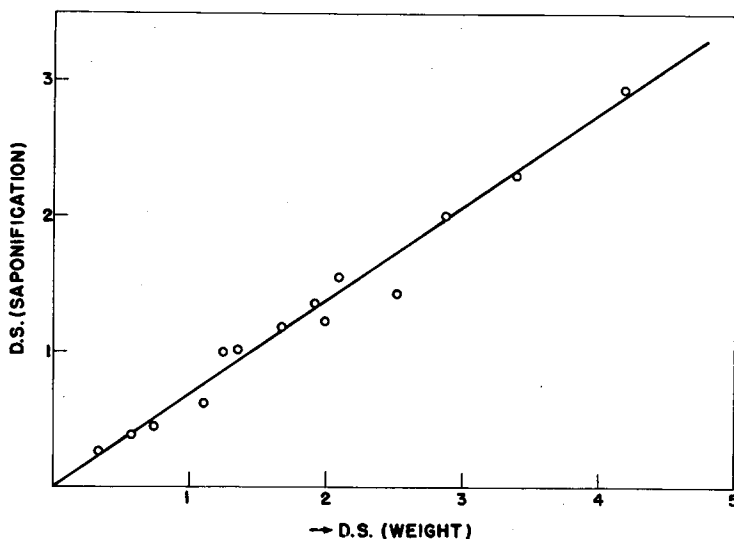


Fig. 1. Relationship between DS by weight gain and by saponification.

correspond to the composition as predicted by their DS values if only cellulose propionate were produced.

It will be observed that the samples 11 and 12 (Table I) have almost the same degrees of substitution by both weight gain and by saponification. This shows that under the conditions specified the side reaction is absent.

All samples prepared in the present study showed an extra peak in their gas-liquid chromatograms except those prepared by the propionic anhydride-propionyl chloride method (samples 11 and 12). A sample supplied by St. Mard et al.⁵ which was prepared by using an equivolume mixture of propionic anhydride and pyridine containing 2% potassium propionate did not show any extra peak.

Characterization of the Product

Attempts to ascribe the extra component to the presence of some contaminant in one of the reagents were unsuccessful, as the chromatograms of pyridine, pyridine hydrochloride, and DMF did not contain the extra peak. Elemental tests showed the absence of chlorine and nitrogen. Absence of the latter was further confirmed by application of the Dumas microdeterminations for nitrogen. These definitely ruled out the possibility of any side reaction of pyridine or DMF to form a complex which might be deposited on the fiber.

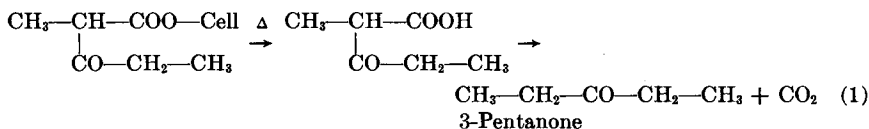
To identify the substance or substances which give rise to the extra component in the propionylation reaction, samples of cellulose propionate were prepared by reacting propionyl chloride with cotton cellulose in a medium of DMF, triethylamine or α -picoline. The chromatograms showed the extra peak only in the case of α -picoline. Since the facts already cited

show that the reaction media leading to formation of the unknown component always contained pyridine or a pyridine derivative and propionyl chloride, it is inferred that the side reaction is probably the outcome of a secondary reaction with the acid chloride complex of organic bases like pyridine or α -picoline.

Malm et al.,¹ in their study of the aliphatic acid esters of cellulose, stated that the use of pyridine and propionyl chloride beyond certain proportions gave products low in propionyl content and with melting points considerably below 230–250°C., considered normal for tripropionates.⁴ In the present case, however, this optimum concentration was exceeded in an attempt to insure full substitution in the heterogeneous phase.

Malm indicated the possible presence of higher acyl groups, such as α -propionylpropionyl, arising from a side reaction or water-soluble impurities, inasmuch as the water tolerance value which is an indication of the nature and number of acyl groups attached to the cellulose had been found to be low. In an attempt to determine the presence of α -propionylpropionyl, an infrared spectrum of sample 10 was compared with that of the sample prepared by St. Mard et al.⁵ Both the samples gave absorptions for CH₂, CH₃, and C=O (ester). An additional peak for hydrogen-bonded OH was observed in the St. Mard sample, indicating the presence of residual cellulosic hydroxyl groups which were absent in the first sample. However, only a faint indication of C=O (ketone) was observed in sample 10.

It was surmised that pyrolytic decomposition of cellulose propionylpropionate in the gas-liquid chromatograph would produce 3-pentanone as shown in eq. (1).



It was found that if 3-pentanone is injected in the chromatograph, it gives a peak at the same retention time as the observed extra peak. The gas-liquid chromatographic experiment was repeated with two other columns containing Carbowax 20M or diisodecyl phthalate on Chromosorb W in order to change the elution characteristic of the components. It was found that both 3-pentanone and the extra component showed the same relative retention time in all the columns, although different columns changed the retention times considerably. This was additional evidence that the extra peak arises from the α -propionylpropionyl moiety produced by the side reaction.

In order further to confirm this conclusion, arrangements were made to collect a larger quantity of the particular compound, giving rise to the extra peak. The chromatographic pyrolysis experiment was repeated a number of times, and the component producing the peak under study was accumulated in carbon tetrachloride, cooled in an ice-acetone bath. Infrared

spectra of 3-pentanone and the above solution are shown in Figure 2. These are similar in all respects except that there is a small additional band in the sample solution, recovered from the chromatograph at 1245 cm.^{-1} , due presumably to propionic acid. The presence of the propionic acid may be due to the fact that in one of the collection runs the peaks for the unknown compound and the propionyl group were not separated sufficiently and the components were collected together.

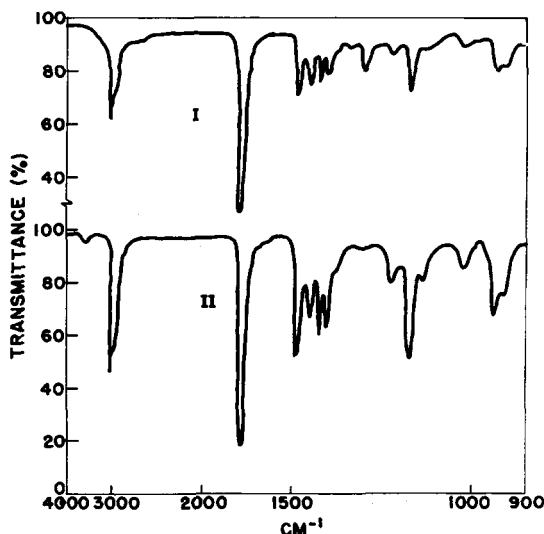


Fig. 2. Infrared spectra of (I) 3-pentanone and (II) the liquid collected from the sample.

As further supporting evidence, the corresponding NMR spectra which are relatively free from the interference of the functional group, were obtained; these are reproduced in Figure 3. The NMR spectra give conclusive evidence that the unknown component collected from the gas chromatograph is 3-pentanone, since both the chemical shifts and methylene-methyl proton ratio correspond to those of 3-pentanone.

Anomaly in DS by Weight and by Saponification

The incorporation of the α -propionylpropionyl group arising from a side reaction along with the propionyl groups indicates the source of the discrepancies in DS determined by saponification and by weight gain. Since the weight of propionylpropionyl is double that of the propionyl group, extra weight comes into play in the determination of DS by weight gain. On the other hand, the DS by saponification will remain unaffected by the extra weight, since only one acidic group is split up by saponification irrespective of whether a propionylpropionyl or a propionyl group is present. DS will, therefore, be different if the substitution takes place both by propionyl and propionylpropionyl groups.

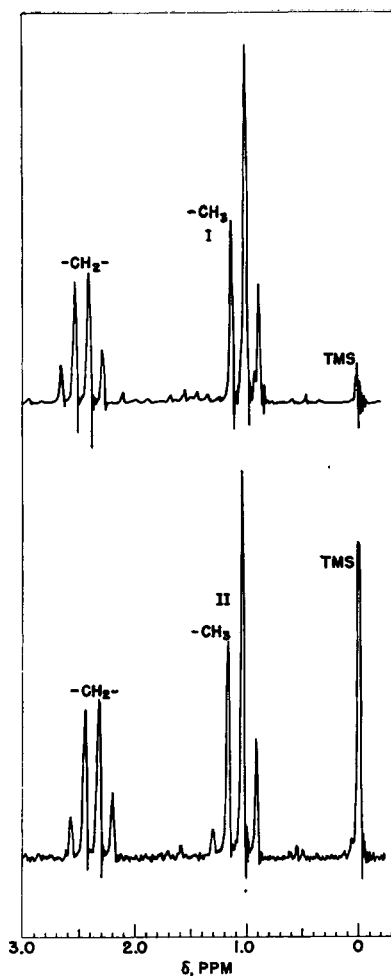


Fig. 3. NMR spectra of (I) 3-pentanone and (II) the liquid collected from the sample.

In determining the relative contribution to the DS by the propionyl and the α -propionylpropionyl species, it was assumed that the α -propionylpropionyl species is stable to the mild alkaline conditions of saponification. Different known amounts of propionic acid were injected into the GLC. The integrated areas of the propionic acid peaks were linearly related to the quantity of propionic acid injected. The calibration curve (Fig. 4), which resulted from this experiment could, therefore, be used for the determination of propionic acid in the unknown samples. This was verified by the estimation of the propionyl group in the St. Mard sample, which agreed very closely with the value reported.⁵ The percentage of propionyl group in the experimental samples was then estimated by repeating the gas chromatographic experiment (Table I). From this and the known weight gain, the proportional contribution of the propionyl and the α -propionyl-

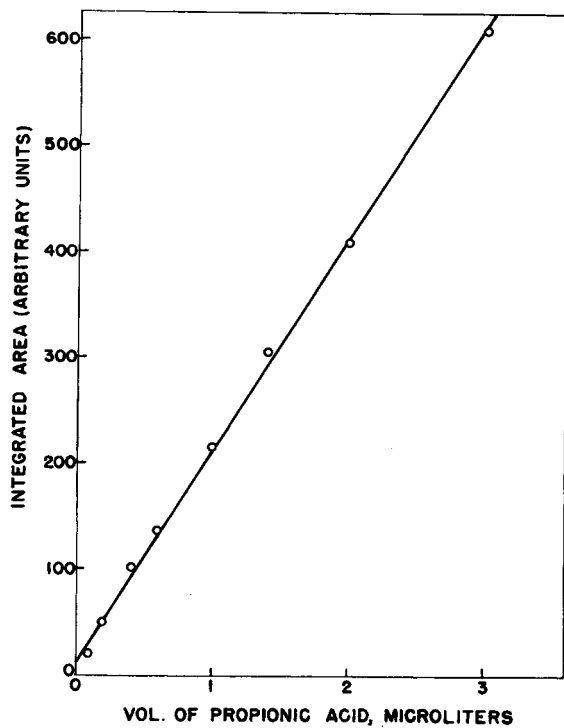


Fig. 4. Least-square fit of the data for the determination of propionic acid by gas-liquid chromatography.

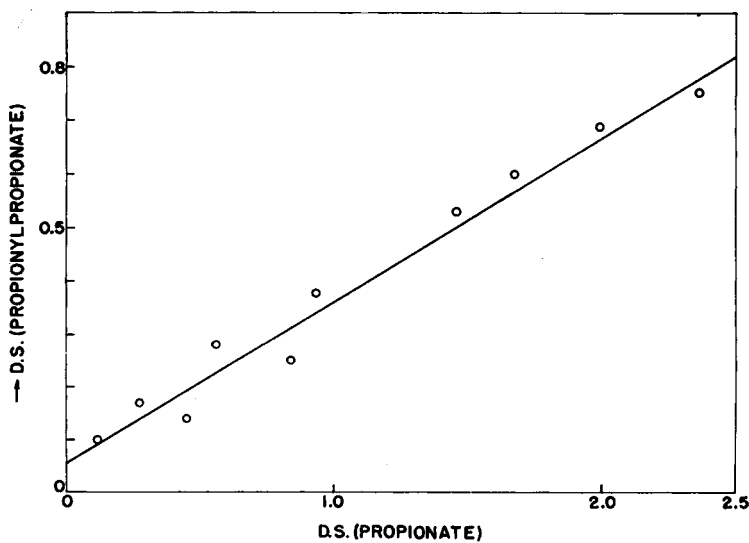
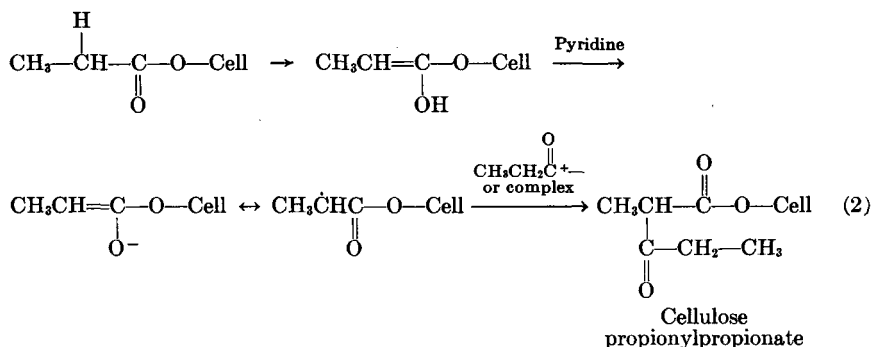


Fig. 5. Least-square fit of the DS by propionyl vs. α -propionylpropionyl groups.

propionyl to the DS could be calculated (Table I). It may be seen that the total DS (given in the last column of Table I), which is the sum of DS as propionate and α -propionylpropionate corresponds well with that by saponification. A plot of DS as propionate versus DS as propionylpropionate shows a linear relationship (Fig. 5), and it is observed from the slope that on the average for every four substituent groups, one is α -propionylpropionyl.

Mechanism of Formation of Propionylpropionate

Since the propionylpropionate is formed only in relatively strong alkaline media, such as pyridine or α -picoline, a mechanism for its formation is suggested on the basis of abstraction of a proton from the cellulose propionate already formed to give the pyridinium ion. The negative center on the carbon α to the ester group then attracts the electrophilic $\text{CH}_3\text{—CH}_2\text{—C}^+\text{=O}$ group to form the propionylpropionate as shown in eqs. (2).



CONCLUSION

The side reaction producing α -propionylpropionyl groups starts at early stages of the esterification. The side reaction takes place only in presence of an organic base like pyridine or α -picoline. The extent of the side reaction is about one-fourth of the total at all degrees of substitution.

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Résumé

Dans la réaction de la fibre de cellulose de coton avec le chlorure de propionyle dans un milieu pyridine-DMF, le degré de substitution, basé sur le gain en poids, était beaucoup plus élevé que celui basé sur la saponification. Des chromatogrammes gaz liquide des produits de pyrolyse montraient un pic supplémentaire. Celui-ci a été identifié comme celui de la 3-pentanone, qui résulte de la pyrolyse à l'acide α -propionylpropionique, substance qui a été proposée par Malm et ses collaborateurs, comme produit secondaire possible. Cette conclusion a été en outre confirmée par spectrométrie infrarouge et NMR du liquide qui a été collecté par fractionnement d'échantillons pyrolysés. La chromatographie gaz liquide quantitative a montré que un des quatre groupes hydroxyles est substitué par un groupe α -propionylpropionyle, la reste étant des groupes propionyles. Un mécanisme possible pour la réaction secondaire est proposée.

Zusammenfassung

Bei der Reaktion von Baumwollcellulosefasern mit Propionylchlorid in Pyridin-DMF erwies sich der Substitutionsgrad auf Grund der Gewichtszunahme als bedeutend höher als auf Grund der Verseifung. Gas-Flüssig-Chromatogramme der Pyrolyseprodukte der Proben zeigten ein Extra-Maximum. Dieses wurde als 3-Pentanone identifiziert, das durch Pyrolyse von α -Propionylpropionsäure entsteht, einer Substanz, die von Malm und Mitarbeitern als mögliches Nebenprodukt angenommen worden war. Diese Annahme wurde weiters durch die Infrarot- und NMR-Spektren der bei der Pyrolyse der Probe in Fraktionen aufgefangenen Flüssigkeit bestätigt. Quantitative GLC zeigte, dass eine von je vier Hydroxylgruppen mit einer α -Propionylpropionylgruppe substituiert ist und der Rest mit Propionylgruppen. Ein möglicher Mechanismus für die Nebenreaktion wird vorgeschlagen.

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