

PREPARATION OF CELLULOSE ACETATE

WITH  
ACETIC ACID



by

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Cambridge, Mass.

May 16, 1935

Professor Ralph G. Hudson  
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Dear Sir:

Enclosed herewith is the thesis entitled " PREPARATION  
OF CELLULOSE ACETATE WITH ACETIC ACID " submitted as partial  
fulfillment of my requirements for the degree of Bachelor of  
Science.

Very truly yours,

Edward H. Taubman

202274

A C K N O W L E D G E M E N T

The author wishes to express his sincere appreciation to Professor Avery A. Morton for his unfailing interest and aid in this investigation.

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T A B L E O F C O N T E N T S

	<u>PAGE</u>
INTRODUCTION - - - - -	1
PURPOSE - - - - -	2
SCOPE - - - - -	2
METHOD - - - - -	2
RESULTS - - - - -	3
CONCLUSIONS - - - - -	3
RECOMMENDATIONS - - - - -	4
 BODY OF REPORT - - - - -	 5
DISCUSSION OF RESULTS - - - - -	6
DESCRIPTION OF RUNS - - - - -	9
 APPENDIX - - - - -	 12
SUMMARY OF DATA - - - - -	13
DESCRIPTION OF APPARATUS - - - - -	14
DESCRIPTION OF REAGENTS - - - - -	15
METHOD OF PROCEDURE - - - - -	16

I N T R O D U C T I O N

## P U R P O S E

The purpose of this thesis is to investigate the possibility of acetylating cellulose with acetic acid and HCl gas at a low temperature, permitting a strong solution of hydrochloric acid. Cellulose is one of the most difficult as well as one of the most important substances to be subjected to acetylation.

## S C O P E

Commercially, cellulose is acetylated by using acetic anhydride, glacial acetic acid, and various catalysts. The cost of the anhydride prohibits a large production because of the cheaper method of plasticizing cellulose through the viscose process.

This investigation, because of lack of time, has been limited to exploring only a few of the many variables affecting the reaction, viz: effect of time, ratio of acid to cellulose, type of acid, and concentration of water. The action of catalysts has been entirely omitted, as well as varying the temperature.

## M E T H O D

The research in its broadest aspects is a study of acylation under the influence of strong solutions of HCl. The desired strength of acid is achieved in two ways, viz: by use of an acid solvent such as glacial acetic acid and by use of low temperatures which permit of higher concentrations of HCl.

R E S U L T S

1. As a result of the acetylation there is definite qualitative proof that a substance soluble in acetic acid is found which precipitates upon dilution. Furthermore this occurred even when there had been no chance for degradation.
2. Except for runs no. 5 and no. 7, definite saponification figures were reached that ranged in acetate value from .18 to .62
3. Qualitatively, preshredding of the cellulose seems to further the reaction.
4. Change of acetylating solution gave a larger acetate value by one-third.
5. Neither time nor doubling the quantity of acid have an appreciable effect on the reaction.

C O N C L U S I O N S

1. That it is possible to acetylate cellulose using only acetic acid and HCl gas, at low temperatures.
2. That at the present stage of the investigation results do not warrant reporting an acetate value above .5.
3. That neither time nor the quantity of the acid have an appreciable effect on the reaction.
4. That preshredding indicates a furtherance of the reaction.
5. That, tentatively, changing the acetylating solution increases the amount of reaction by approximately 30%.



R E C O M M E N D A T I O N S

1. That the complete set of variables influencing the reaction be investigated thoroughly as to their effects.
2. That the influence of catalysts on the reactions be particularly investigated.
3. That the solubility of cellulose acetate with acetate values of 2.5 and below in various solvents be investigated.
4. That pre-treatment of the cellulose be tried, as for instance, refluxing in acetic acid.
5. That the solubility of cellulose acetate in glacial acetic be determined.

B O D Y O F R E P O R T

DISCUSSION OF RESULTS

The principal result of the present investigation was to prove the possibility of acetylating cellulose with 100% HAC and HCl gas at low temperatures. Certainly the acetate values as calculated are beyond experimental error, although part of this value probably is due to degradation in some of the runs. It is the author's opinion that the acylating mixture exerts a combination of four influences. First, both the acetic acid and the HCl have a strong affinity for water, thus exerting a dehydration<sup>1</sup> action that aids the spitting out of a molecule of water when cellulose acetate is formed. Second, the HCl forms some acetyl chloride with the acetic acid, which in turn has a powerful affinity for water. Third, the HCl acts as a condensing agent in the formation of cellulose acetate. And finally, the HCl has a catalytic action.

A mixture of acetic acid and acetyl chloride has been shown to acylate cellulose after a few days. <sup>1</sup>The product was dark colored and contained chlorine. Other mixtures have been tried using chloroacetyl chloride <sup>2</sup> and increasing the acidity <sup>3</sup>. However, no previous experimenter has worked at such low temperatures as in the present investigation, that permit such terrific concentrations of HCl.

Because of the many variable factors influencing this reaction, time did not permit a complete investigation, and even the preliminary results found should be thoroughly checked. Time, temperature, ratio of acid to cellulose, rate of reaction, equilibrium, and catalysts all influence the reaction to a more or less degree. The results tend to show that time does not

1 Groggin - Unit Processes

2 Barnett, J. Soc. Chem. Ind. 40 253-6T (1921)

3 Conant and Bramann, J. Am. Chem. Soc. 50 2305 (1925)

have an appreciable effect on amount of reaction. Also that the renewal of the HAC increases the reaction by one-third. Qualitatively, pre-shredding of the cellulose tends to help the reaction. These points will be brought out more forcibly by analyzing each run separately.

Runs no. 1 and 2

No. 1 run differed from no. 2 only in the length of time. No. 2, in fact, gave a 16% greater acetate value. Since they were made together and underwent the same conditions, even though there were an error in the analysis, the results would still give a comparative value. Cork stoppers being used when shaking up the saponification mixtures, undoubtedly adsorbed some NaOH, thus accounting somewhat for the higher acetate values in comparison with the other runs. These two runs tend to show that time is a negligible factor, after a certain minimum period, in the amount of reaction, and a large enough time might even be a deterrent to it. It would be quite interesting to determine this minimum time.

Runs no. 3,4,5, and 6

These runs were made with the view of checking up on the effect of time and the type of acid. It has been shown that acetic acid distilled over  $P_2O_5$  will give some acetic anhydride, although only in minute quantities. Therefore some twice distilled acid over  $P_2O_5$  was used in no. 3 and 5, and some fractionated HAC in no. 4 and 6. Unfortunately a combination of errors and accidents in these four runs make the results inconclusive. Run no. 5 was broken before completion; no. 6 was allowed to stand 3 days before filtering, permitting degradation; and no. 3,4, and 6 were saponified with  $Ba(OH)_2$  by mistake instead of NaOH. Thus

the results may be disregarded except in so far as they show acetylation.

Run no. 7

This run was made with the view of determining the minimum time necessary to acetylate the cellulose to a possible maximum. Unfortunately an accident in the centrifuge while washing the residue completely scattered the mixture beyond hope of using it.

Runs no. 8 and 9

The previous low acetate values arrived at produced speculation on two points. First that the cellulose acetate might have a limited solubility in the acetic acid, and second, that the spitting out of  $H_2O$  on the formation of the acetate diluted the solution so that an early equilibrium was reached. These two runs attempted an investigation into these two possibilities. Run no. 8 used the same amount of cellulose as formerly but doubled the amount of acid used. Run no. 9 was acetylated twice using 2-10 cc. portions of acid on the same cellulose. The results tend to show that there is more basis to the second speculation than the first. A check up is strongly adviseable however.

The above results, while not extremely conclusive, and even if true, not very exciting, do show something never before accomplished: the acetylation of cellulose without acetic anhydride or acetyl chloride. Future investigators will have the opportunity of endeavouring to increase the yield by permitting fewer mistakes and changing the previously mentioned variables.

D E S C R I P T I O N O F R U N S

Run no. 1

This was started on April 24 but was not taken below room temperature that day. On April 25, it was taken down to  $-20^{\circ}\text{C}$  but lack of time prevented completing the run. However, on April 26 the run was completed for 8 hours at  $-40^{\circ}\text{C}$ . The apparatus was then removed from the  $\text{CO}_2$  bath and allowed to warm up. It was quite cloudy and slightly yellowish. The run was filtered next morning (April 27). The filtrate upon dilution was quite cloudy and when centrifuged after standing a couple of days gave a flocculent precipitate. Water was added to the residue remaining after the filtration, and the suspension then washed into a test-tube. The residue was quite broken up. Following repeated washing until the residue had a pH between 6.2 and 7.0, it was saponified and the number of milliequivalents of base used for saponification determined. A weighed amount of the residue was used for this saponification. A cork stopper was used when shaking up the saponification mixture. 10.0 cc. HAc distilled over  $\text{P}_2\text{O}_5$  was used for the acylating solution.

Each of the following runs was conducted substantially the same as no. 1, but for the exceptions as noted. These exceptions are summarized in the summary of data sheet.

Run no. 2

This run was made along with no. 1 during the same time, except that it was only 4 hours long at  $-40^{\circ}\text{C}$ . The residue did not appear as well broken up as no. 1 when placed into water. The test-tube holding the diluted filtrate broke when centrifuging so that it could not be determined if there was a precipitate.

The solution was definitely cloudy though. In both this and the previous run HAC distilled over  $P_2O_5$  was used.

Run no. 3

This run was completed in one day, including the filtration. Before acylation, however, the cellulose was thoroughly shredded. This is true also of all the succeeding runs. The acid used here was distilled twice over  $P_2O_5$ . The time of the run was 4 hours at  $-40^\circ C$ . The diluted filtrate was quite cloudy; even more so than nos. 1 and 2. When a portion of the residue was saponified,  $N/10 Ba(OH)_2$  was used by error instead of  $N/2 NaOH$ . This happened also in runs no. 4 and 6. A rubber stopper was used in this and succeeding runs when shaking the saponification mixture.

Run no. 4

This run was conducted at the same time as no. 3, along identical conditions, except for the fact that HAC fractionated from  $99\frac{1}{2}\%$  HAC was used instead of the former. The diluted filtrate seemed to be cloudier than no. 3. The acetylating mixture was stirred two or three times during the course of the run.

Run no. 5

The apparatus broke in this run after  $3/4$  of the 8 hour period had elapsed. HAC distilled twice over  $P_2O_5$  was being used.

Run no. 6

This run was completed on May 3, but was allowed to stand 3 days until May 6 before filtration. During this period the solution turned definitely yellowish. HAC fractionated from  $99\frac{1}{2}\%$

HAc was used. The diluted filtrate gave a considerable precipitate upon centrifuging. The residue was more broken up than in any previous run, when placed in water. Saponification was done by error with  $\text{Ba}(\text{OH})_2$  as in nos. 3 and 4. This was an 8 hour run.

Run no. 7

This run was made to determine the effect of time on the acetate value. Unfortunately the test-tube holding the residue was broken in the centrifuge, thus spoiling the run. The diluted filtrate showed some cloudiness but not as much as in previous runs.

Run no. 8

This run was made with double the amount of acid used on previous runs, that is 20 cc., and continued for 4 hours. The diluted filtrate was quite cloudy but gave no precipitate upon centrifuging.  $\text{N}/2$  NaOH was used for saponification.

Run no. 9

This run was split into 2-2 hour periods using 10 cc. HAc in each. The solution was filtered after each period and the same cellulose used again. The two diluted filtrates had a cloudiness of about the same degree and gave no precipitate upon centrifuging.



A P P E N D I X

S U M M A R Y O F D A T A

Run No.	Acetate Value	Brief Description of Run	Type of Acid Used	Time of Run Hrs.	Time before Filtering	Wt. of Cellulose in Gun	Amount of Acid Used CC.	Wt. of Material Used for Sapon.	Mil. Equiv. Material for Sapon.	Mil. Equiv. Excess OH	Sapon Agent
1.	.53	Cell. in Hac 2 days before acylation. Cellulose appeared broken up at end of run	Hac distilled once on P <sub>2</sub> O <sub>5</sub>	8	Over-	.1716	10.0	.0588	.363	.193	N/2 NaOH
2.	.62	Almorethan 2		4	night	.1642	10.0	.0425	.262	.162	N/2 NaOH
3.	.19	Shredded cellulose before use.	Hac twice distilled over P <sub>2</sub> O <sub>5</sub>	4	None	.20	10.0	.1496	.923	.171	N/10 Ba(OH) <sub>2</sub>
4.	.18	Diluted filtrate had definite #4 more than	ionated from C.P. 99% Hac	4	None	.20	10.0	.1380	.852	.155	N/10 Ba(OH) <sub>2</sub>
5.	--	Apparatus broke after 3 hrs. spoil run.	Hac twice distilled over P <sub>2</sub> O <sub>5</sub>	6	---	.20	10.0	---	---	---	---
6.	.56	Degradation occurred on long stand ing.	Hac Fractionated from 99 1/2% Hac	8	3 Days	.20	10.0	.0890	.549	.306	N/10 Ba(OH) <sub>2</sub>
7.	--	Diluted filtrate small bloudiness. used twice		2	None	.20	10.0	---	---	---	---
8.	.30	amt. acid noticeable effect.		4	None	.20	20.0	.0932	.575	.173	N/2 NaOH
9.	.46	split run in 2 parts, replacing Hac on same cell		2 + 2	None	.20	10.0 + 10.0	.1326	.818	.376	N/2 NaOH

MISCELLANEOUS: Cellulose used in #3 run and afterwards was shredded before using. Ba(OH)<sub>2</sub> was used as a saponifying agent in runs #3, #4, and #6 by error.

D E S C R I P T I O N O F A P P A R A T U S

The HCl was generated in a 2 liter distilling flask with two 500cc. separatory funnels holding the  $H_2SO_4$ . The gas then separated into two lines controlled by glass stop-cocks, and thence passed through an Erlenmeyer flask holding the drying acid, before entering the acylating apparatus. Control of the flow of gas was easy because of the stop-cocks on the line and in the funnels. Rubber stoppers only were used in the apparatus.

The acylating apparatus is better shown than described. It is at present (May, 1935) being held by Professor A.A. Morton of the chemistry department. Fittings are of ground glass. An extra opening is provided in the event it is found advisable to pass CO through with the HCl.

The HCl gas comes in through the acylating mixture by means of one of the top openings. After passing through the solution it passes out through the lower side arm.

D E S C R I P T I O N O F R E A G E N T S

HCl - This was prepared by dropping C.P.  $H_2SO_4$  sp.gr. 1.84 on ordinary salt and leading it through the same kind of  $H_2SO_4$  to dry it.

CELLULOSE - Ordinary cotton was used , kept in a bottle over  $P_2O_5$ .

HAc - Runs no. 1 and 2 used ordinary glacial acetic acid distilled over  $P_2O_5$  (1/4 lb. for 2 lit.), taking the fraction boiling at  $117^\circ C$ . About  $1\frac{1}{2}$  liters were obtained from 2 liters. The acid was refluxed for 2 hours before distillation. The distillation took place through a Widmer column.

Runs no. 3 and 5 used this same HAc distilled once more over  $P_2O_5$  under the same conditions.

The remainder of the runs used HAc fractionated from C.P. (Malinkrodt) 99 1/2% HAc in a Widmer column. 190 cc. out of 400 cc. were obtained at  $117.9^\circ C$  when the barometer was 757 mm.

NaOH - 1.243 N

NaOH - 0.1116N

$H_2SO_4$  - 1.336 N

Standardized in March, 1935 by

P. Kurz

METHYL RED

PHENOLPHTHALEIN

Indicating solutions

DISTILLED WATER only was used in washing and dilution.

M E T H O D O F P R O C E D U R E

Cellulose, dried over  $P_2O_5$ , was weighed out roughly to approximately .20 grams. In no. 3 and succeeding runs it was then shredded before being placed in the acylating apparatus. 10.0 cc. of acid (except in no. 8 run) were then added from a burette. This mixture was then saturated at room temperature before being gradually reduced to  $-40^{\circ}C$ . This is absolutely necessary or else the acetic acid will freeze preventing the passage of the gas. The solution was kept at  $25^{\circ}C$ ,  $0^{\circ}C$ , and  $-20^{\circ}C$  for  $5/4$  hour each for this saturation. These times were arbitrarily selected and possibly a shorter time would do. Time, however, did not permit this investigation. The time of the run was calculated from when the temperature reached  $-40^{\circ}C$ . The apparatus was placed in a thermos bottle containing standard freezing mixture and solid  $CO_2$  added to regulate the temperature. This temperature of  $-40^{\circ}C$  was chosen arbitrarily, although previous experimentation by Abramowitz '35 tended to show reaction at this point with acetyl chloride in acetic acid. During the run the temperature was allowed to rise to  $-35^{\circ}C$  and then enough  $CO_2$  added to lower it again to  $-45^{\circ}C$ . Because of the thermos bottle, however, the temperature remained sensibly constant.

At the end of the run the apparatus was withdrawn from the thermos bottle and allowed to warm up to room temperature. The dissolved HCl which had almost doubled the volume of the acylating solution came off in great quantities during this time. Following this the mixture was filtered through ordinary

filter paper and the filtrate diluted. Cellulose will not dissolve in strong HAc but cellulose acetate will. However, dilution of the acid will throw out the acetate. Therefore this dilution is a good qualitative test for the acetate.

In order to saponify the acetate residue it must first be washed free of acid. This was accomplished by shaking up with distilled water, centrifuging the suspension, decanting, and repeating this until the decantation liquor made methyl red indicator yellow. This meant the pH was above 6.2. The residue was then washed successively with alcohol and ether and left to dry overnight in an oven at 120°C. The saponification was then carried out by the method used by E. Knowenagel and K. Konig described on p.273 in "Methods of Cellulose Chemistry", Chas. Dorée, D. Van Nostrand Co. Inc. 1933.