

THE ROLE OF ACID CATALYSTS IN THE MANUFACTURE OF CELLULOSE ACETATE

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INTRODUCTION

Commercial processes for the manufacture of cellulose acetate depend on the reaction of an activated cellulose with acetic anhydride using a strong acid catalyst. (i) Activation of the cellulose implies swelling to make internal surfaces accessible to the acetylating agents. (ii) Though many acid catalysts have been considered, only sulphuric and perchloric acids have practical significance. (iii) The acetylation may be conducted in a nonsolvent diluent, whereupon the cellulose triacetate retains the fibrous form of the original cellulose. (iv) The reaction medium may contain a cellulose acetate solvent, e.g. methylene chloride and/or acetic acid. In this case, the progress of the reaction is readily apparent as the acetylated product dissolves in the reaction medium.

There are many reasons for desiring to measure the reactivity of a cellulose sample in the acetylation reaction. For example, it would be useful to (a) Compare cellulose samples from different sources. (b) Study the effects of pulping variables. (c) Assess the effectiveness of cellulose activating (swelling) procedures. (d) Study the chemical reaction kinetics to elucidate aspects of the acetylation mechanism.

To this end, many investigators have reported acetylation test procedures. Borgin¹⁻³, Blume and coworkers⁴, Malm and coworkers⁵, Akim⁶, Laamanen and Sihtola⁷, and Frith⁸ have made significant literature contributions recently in this field. Rosenthal and White have previously reported⁹ in detail on an optical procedure for quantitative acetylation of cellulose which offers some interpretive advantages over other reported procedures.

ACETYLATION RATE PROCEDURE

The quantitative acetylation procedure consists of reacting a preswollen cellulose sample with acetic anhydride and sulphuric acid at relatively high dilution (~ 2 per cent cellulose) in acetic acid. The reaction is conducted isothermally in a stirred flask immersed in a constant temperature bath. The reaction is followed by measuring the light transmission of aliquots removed at intervals. *Figure 1* shows the arrangement for light transmission measurements; the ratio of transmission readings at two positions, T_A/T_B , is designed to maximize the light scattering effect of undissolved cellulosic fragments while eliminating the effect of extraneous colour absorption. The

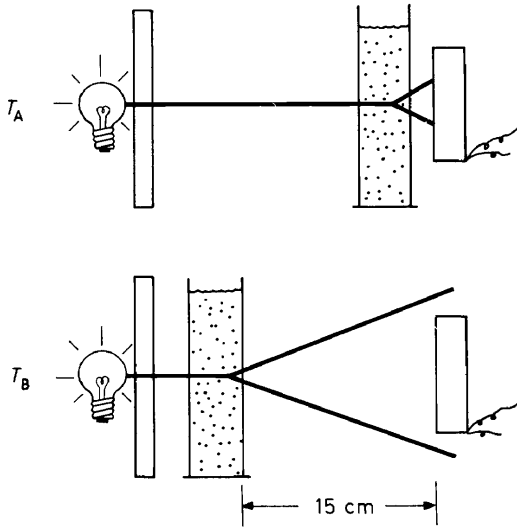


Figure 1. Arrangement for light transmission measurements

previous paper⁹ showed that over the range 0.0–0.4 per cent cellulose (Figure 2) the Beer–Lambert relationship was applicable, i.e.

$$\log \left[\frac{T_A}{T_B} \right] = kc \quad (1)$$

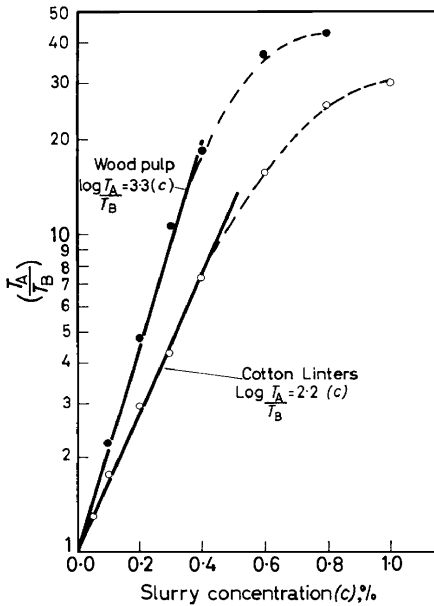


Figure 2. Light transmission calibration

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in which the value of k for cotton linters = 2.2 dl/g, and for wood pulp = 3.3 dl/g.

If the rate of dissolution is proportional to the amount remaining, i.e. first order kinetics apply, one would expect a straight line plot of $\log (c)$ versus time. Incorporating equation (1), one would expect a straight line plot of $\log [\log (T_A/T_B)]$ versus t .

A check of the calibration procedure was made by conducting an acetylation in which 0.023 g of unpretreated cotton linters was mixed with 2.0 g of pretreated cotton linters at the start of the acetylation reaction. The total volume of the reaction mixture was 200 ml. The optical transmission data are given in Table 1. By plotting $\log (T_A/T_B)$ versus time on semilog co-

Table 1. Acetylation clearing rate data

[2.0 g Pretreated cotton linters: 0.023 g Unactivated cotton linters]

| Time (min) | T_A | T_B | $\log T_A/T_B$ | $\log T_A/T_B$ (Corrected For Blank) |
|------------|-------|-------|----------------|---|
| 13 | 79.8 | 8.5 | 0.973 | 0.964 |
| 20 | 93.7 | 39.1 | 0.379 | 0.370 |
| 24 | 97.7 | 80.5 | 0.084 | 0.075 |
| 29 | 98.4 | 90.0 | 0.039 | 0.030 |
| 34 | 98.8 | 92.0 | 0.031 | 0.022 |
| 39 | 97.6 | 89.7 | 0.037 | 0.028 |
| 43 | 98.4 | 91.8 | 0.030 | 0.021 |
| 57 | 98.5 | 91.5 | 0.032 | 0.023 |
| Blank* | 100.0 | 97.8 | 0.009 | — |

* Blank refers to cell containing liquid reagent without cellulose present.

ordinate paper (Figure 3) a sharp break is observed at $\log (T_A/T_B) = 0.0255$ which is equivalent to 0.023 g of cellulose in suspension.

This paper summarizes some key observations on cellulose activation and acetylation kinetics which were revealed by application of this procedure.

CELLULOSE ACTIVATION

The function of the activation process is to increase the accessibility of the cellulose hydroxyl groups to the acetylating agents. The rate of diffusion and the extent of swelling are functions of the swelling agent, cellulose state, temperature, and time.

A small molecule facilitates diffusion. Further, if the molecule is polar, it can disrupt strained secondary valency bonds, thus permitting greater swelling. Water is the ideal swelling agent because of its molecular size and polarity. Since water would consume the acetic anhydride needed for acetylation, either it must be displaced after it has performed its swelling function or some more practical, if less ideal, liquid should be used. In most cases, acetic acid is as effective a swelling agent as water with regard to extent of swelling, slower than water with regard to rate of swelling. The presence of a small amount of water to act as a wedge accelerates the swelling with acetic acid.

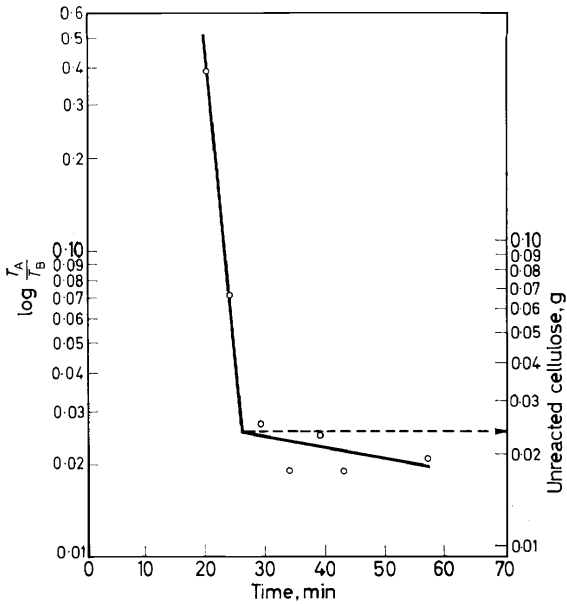


Figure 3. Acetylation rate

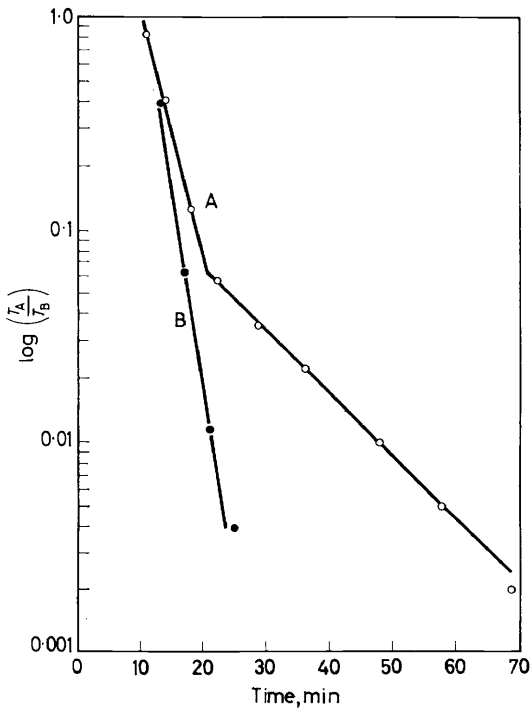


Figure 4. Acetylation rate [A: pretreated 4 min at 25°C. B: pretreated 6 min at 25°C]

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Table 2 summarizes the reaction conditions for a high dilution acetylation procedure in which the swelling stage consisted of agitation of 4.0 g wood pulp with 1.4 ml of acetic acid for 4 min. The light transmission data are shown as Line A in Figure 4. Note the break corresponding to 0.6 per cent of the cellulose incompletely activated. The same pulp agitated for 6 min

Table 2. Proportions for high dilution acetylation procedure

| | |
|-------------------------|--|
| Swelling Stage | 4.0 g wood pulp (8% H ₂ O) 1.4 ml acetic acid Agitate 4 min at 25°C |
| Catalyst Sorption Stage | 0.30 ml sulphuric acid 2.8 ml acetic acid Agitate 5 min at 25°C |
| Acetylation | 150 ml of 7% acetic anhydride at 45°C |

at 25°C gave Line B, showing complete activation. This approach could be extended to establish minimum activation times under a variety of circumstances.

In much of the work that follows, acetylation rate is characterized by the time to reach a predetermined residue, i.e. 99.9 per cent of the cellulose dissolved. In the case of Curve B in Figure 4, this would be 21 min.

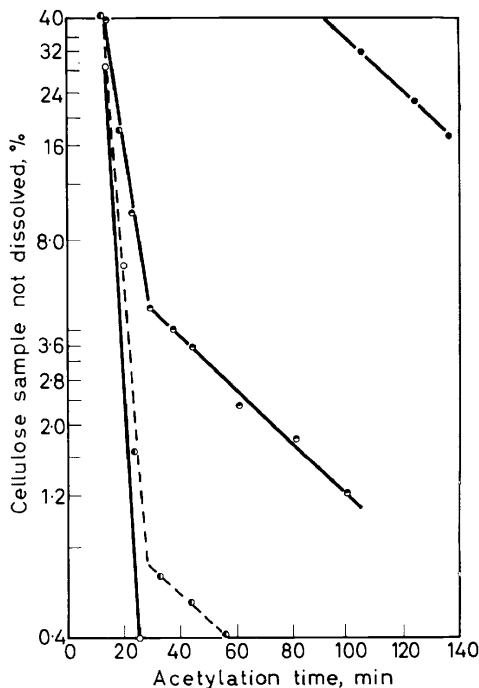


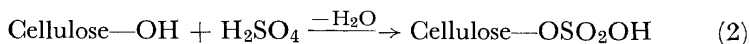
Figure 5. Acetylation rate of undissolved cellulose sample (2.0 g cotton linters + 150 ml acetic acid + 0.2 ml sulphuric acid) after various activation times [Time at 25°C: ● 0.2 h; ● 3.5 h; ● 6.5 h; and ○ 16.0 h]

Occasionally, activation "recipes" suggest the use of sulphuric acid in the acetic acid swelling liquid, presumably to promote cleavage of hydrogen bonds and thus increase swelling. It has been found that if one soaks cellulose in acetic acid containing sulphuric acid, the time required for complete swelling is prolonged considerably. *Figure 5* summarizes the findings. The 16 h requirement is in contrast to the 6 min requirement in the absence of sulphuric acid. It is likely that sulphuric acid is sorbed on the outer surfaces of unswollen cellulose and blocks the pore entrances into the cellulose structure either by actual physical blocking or by an electrical repulsion effect, thus reducing the cellulose swelling rate. The effect is pronounced even at high dilutions of sulphuric acid in acetic acid because of the selective sorption of sulphuric acid by the cellulose.

ESTERS OF SULPHURIC AND PERCHLORIC ACIDS

Sulphuric acid esters

Esters of sulphuric acid are well known and stable compounds. Malm, Tanghe, and Schmitt¹⁰ describe the rapid reaction between methanol and sulphuric acid in acetic acid-acetic anhydride at room temperature. After 30 sec, no free sulphuric acid could be precipitated with barium chloride. This same Eastman Kodak group showed analogous results with cellulose; no sulphur combined during activation, but after the addition of acetic anhydride, the sulphuric acid combined rapidly and quantitatively with the cellulose¹¹.



Perchloric acid esters

Esters of perchloric acid are known; but they are prepared only with great difficulty, e.g. by double decomposition of silver perchlorate with alkyl halides¹², distillation of barium perchlorate with the corresponding alcohol¹³, or by methylating with diazomethane. No evidence has ever been obtained for the formation of a cellulose perchlorate compound during acetylation of cellulose.

TWO CELLULOSE ACETYLATION MECHANISMS

When acetylating with sulphuric acid catalyst, two distinct acetylation mechanisms can be observed, depending on a relatively minor modification of the pretreating procedure as shown in *Table 3*. In the absence of acetic anhydride, sulphuric acid is reversibly adsorbed from acetic acid onto cellulose¹⁴. In the catalyst sorption step (*Figure 6*) it distributes itself on sites throughout the cellulose fibre. In the presence of acetic anhydride, sulphuric acid is chemically bound to the cellulose at such a rapid rate that it cannot migrate into the fibre and is not present therein unless it was there beforehand. Thus in the one stage pretreatment routine, all the sulphuric acid catalyst is bound to the surface of the fibre, and the reaction proceeds from the surface only. In the two-stage pretreatment the catalyst sorbed throughout the fibre permits a more rapid overall reaction. The acetylation

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Table 3. Cellulose activation procedures

| | One-Stage | Two-Stage |
|---|---|---|
| First stage activation (Swelling) | 4.0 g cellulose 1.4 ml acetic acid 15 min at 25°C | Same |
| Second stage activation (Catalyst sorption) | None | 0.30 ml sulphuric acid 2.8 ml acetic acid 5 min at 25°C |
| Acetylation | 0.30 ml sulphuric acid 2.8 ml acetic acid 150 ml 7% w/w acetic anhydride 45°C | 150 ml 7% w/w acetic anhydride 45°C |
| Cellulose | Time For 99.9% Reaction (min) | |
| Cotton linters | 49, 48 | 25, 27 |
| Wood pulp | 33, 33 | 23, 22 |

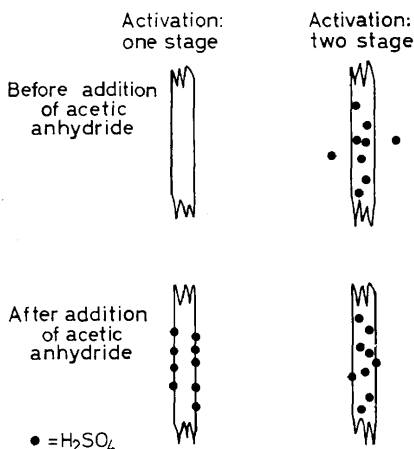


Figure 6. Two acetylation mechanisms

Table 4. Cellulose activation procedures using perchloric acid

| | One-Stage | Two-Stage |
|---|---|--|
| First stage activation (Swelling) | 2.0 g wood pulp 0.7 ml acetic acid 12 min at 25°C | Same |
| Second stage activation (Catalyst Sorption) | None | Perchloric acid as 3% v/v in acetic acid 5 min at 25°C |
| Acetylation | 150 ml 7% w/w acetic anhydride Perchloric acid as 3% v/v in acetic acid 45°C | 150 ml 7% w/w acetic anhydride 45°C |
| Perchloric acid (g) | Time For 99.9% Reaction (min) | |
| 0.18 | 144 | 137 |
| 0.36 | 81 | 84 |

reaction times in *Table 3* show the effect for both wood pulp and cotton linters.

Perchloric acid is not known to combine with cellulose. It was expected that the diffusion of perchloric acid would be equally effective when added with the acetic anhydride as when added in a separate catalyst sorption stage. The data given in *Table 4* show that this is indeed the case.

CATALYST RATIO TO CELLULOSE AND TO TOTAL VOLUME

In *Table 5* the amounts of cellulose and catalyst have been adjusted so as to observe relative acetylation rates as a function of (catalyst/volume) and (catalyst/cellulose). In the sulphuric acid system, the rate increase occurs

Table 5. Cellulose acetylation rates, sulphuric acid versus perchloric acid
[Cellulose activated with acetic acid. Total acetylation reaction volume, 200 ml]

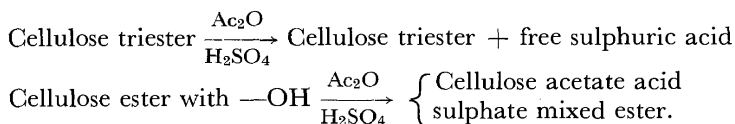
| Cellulose (g) | Catalyst (g) | % Catalyst/Volume | % Catalyst/Cellulose | Acetylation time (min) | Relative rate |
|---------------|-------------------------|-------------------|----------------------|------------------------|---------------|
| 2 | SULPHURIC ACID 0.18 | 0.09 | 9 | 62 | 1.0 |
| 1 | 0.18 | 0.09 | 18 | 34 | 1.8 |
| 2 | 0.36 | 0.18 | 18 | 28 | 2.2 |
| 1 | 0.36 | 0.18 | 36 | 18 | 3.5 |
| 2 | PERCHLORIC ACID 0.18 | 0.09 | 9 | 140 | 1.0 |
| 1 | 0.18 | 0.09 | 18 | 114 | 1.2 |
| 2 | 0.36 | 0.18 | 18 | 83 | 1.7 |

with an increase in catalyst/cellulose ratio; whereas in the perchloric acid system, the rate depends more on catalyst/total volume ratio. Again, this is taken as evidence that the effectiveness of sulphuric acid as an acetylation catalyst is due to its concentration on the cellulose.

Malm *et al.*¹⁵ studied a number of acid catalysts for acetylation of various cellulosic products; they concluded, also, that the effectiveness of sulphuric acid for acetylation of cotton linters was due to its retention on the fibres at the site of acetylation.

CELLULOSE DEGRADATION WITH FREE AND COMBINED ACID CATALYSTS

Malm *et al.* reported on the rates of degradation of cellulose derivatives in acylation media¹⁶. By starting with (a) cellulose triester, (b) cellulose ester with some free hydroxyl, and taking advantage of the rapid reaction of sulphuric acid with cellulose free hydroxyl, they were able to study degradation rates for both free and combined sulphuric acids.



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Their results (Figure 7) showed very much more degradation in the system with combined sulphuric acid. They observed that sulphuric acid

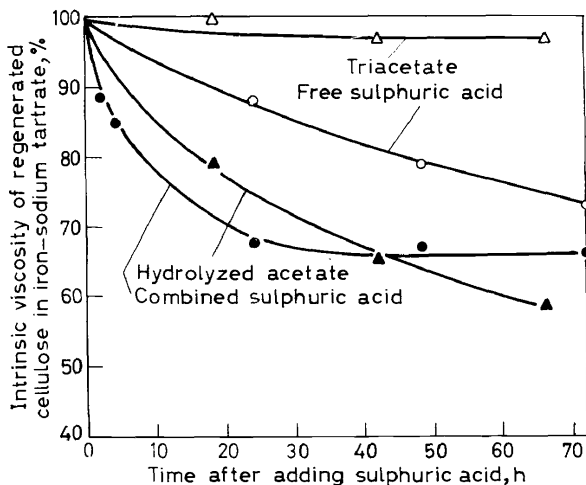


Figure 7. Differences between viscosity reduction of triacetate and acetate sulphate in acetic acid-acetic anhydride [Δ , \blacktriangle 3% anhydride; \circ , \bullet 10% anhydride]

combined with a cellulose ester shows nearly the same acidity function as free sulphuric acid in mixtures containing acetic anhydride, and thus concluded that the cellulose ester with combined sulphuric acid is more susceptible to degradation. Analogous experiments using perchloric acid did not show any differential degradation when using cellulose tripropionates with/without free OH, simply because perchloric acid does not combine with cellulose. It is proposed that this greater susceptibility to degradation is due to the sulphuric acid ester bond constraint that retains the degradation catalyst in close proximity to the cellulose chains.

In 1961 Rosenthal published the unexpected result (cf. Figure 8) that

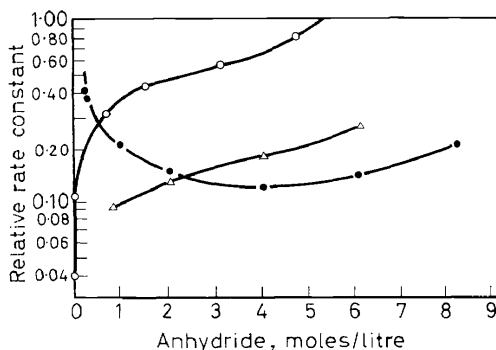


Figure 8. Effect of anhydride concentration on relative rate of degradation ($\text{H}_2\text{SO}_4 = 0.181$ mole/l. at 25°C) [\circ CP in propionic acid; \triangle CP in acetic acid; \bullet CA in acetic acid] CA = Cellulose acetate; CP = Cellulose propionate

the degradation rate of cellulose acetate passed through a minimum at about 40 per cent acetic anhydride, whereas a cellulose propionate system showed a regular increase in degradation over the same anhydride range¹⁸. Malm and coworkers¹⁶ have since pointed out that the cellulose propionate used in that study was a triester, whereas the cellulose acetate contained 0.52 free hydroxyl; as a result, these observations included the effects of free and combined sulphuric acid, the relative amounts of these, and thus the degradation rate, depending on anhydride concentration.

ACETYLATION REACTION MECHANISM

Considerable work has been done on the reaction rate kinetics and mechanism of esterification of alcohols in general¹⁷, and of cellulose in particular⁸. The most plausible mechanism is shown in *Figure 9*. This scheme can be summed up in the rate expression

$$\frac{dx}{dt} = \frac{k [H^+] [Ac_2O] [Cell-OH]}{[AcOH]} \quad (3)$$

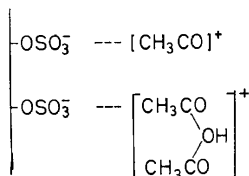
If one is to take into account the information concerning ratio of sulphuric acid to cellulose, this becomes

$$\frac{dx}{dt} = \frac{k [H_2SO_4] [Ac_2O] [Cell-OH]}{[Cellulose]_0 [AcOH]} \quad (4)$$

In equation (4), $[Cellulose]_0$ signifies the initial cellulose concentration, a time invariant parameter, as distinguished from $[Cell-OH]$, which signifies unreacted cellulose hydroxyl groups.

Admittedly, the expression (eq. 4) is a great simplification of the situation which is applicable only over a finite portion of the reaction time scale. It does not include many facets of what is happening, e.g. sulphuric acid esterification, acetate sulphate ester interchange, acetolysis, sulphoacetic acid formation, etc., but it is a description of the principle product forming reaction.

The scheme in *Figure 9* shows that positively charged fragments, e.g. proton, acylonium ion, etc. are involved in the esterification reaction. While a case has been built for the sulphuric acid catalyst functioning from its constrained location on the cellulose fibre, it is only the anion, i.e. $Cell-OSO_3^-$ which is constrained. The implication is, therefore, that the positively charged esterifying agents are themselves not truly free; but they are also constrained to the vicinity of the cellulose by virtue of electrostatic attraction to the bound sulphate anion.



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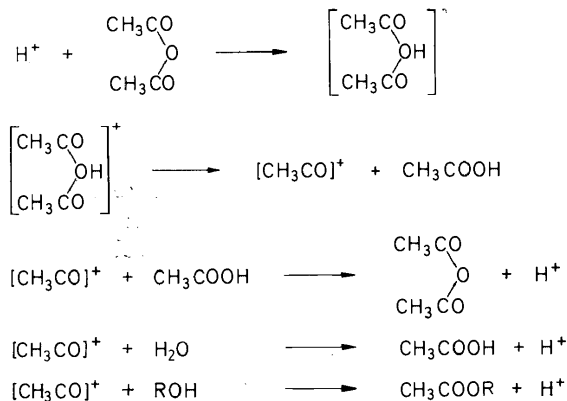
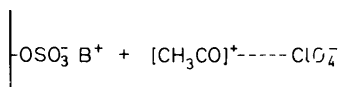


Figure 9. Esterification reaction scheme

The presence of an alternate unbound anion, e.g. an appropriate perchlorate salt, might minimize the constraint of the reactive carbonium ions to the vicinity of the bound sulphate.



This would be predicted to reduce the observed rate of acetylation.

ACTIVATION TEST

The complex role of sulphuric acid in the acetylation reaction led to the development of a diagnostic test for extent of cellulose activation. The data presented suggested that an excess of sulphuric acid, i.e. ~50 per cent based on cellulose, would accelerate the reaction of the activated fraction of the cellulose and would grossly inhibit the acetylation of the fraction which had

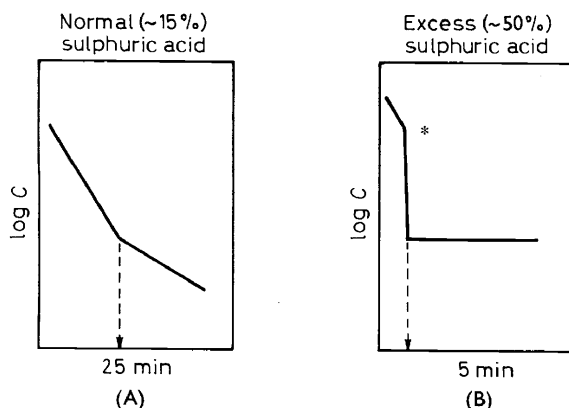


Figure 10. Rapid test for cellulose activation. [The break in Figure (B) indicates a time at which the sulphuric acid was increased to 50 per cent on cellulose; the delay was found empirically to be necessary].

not been activated in the pretreatment. This turned out to be the case. The phenomenon is shown schematically in *Figure 10*. Thus a reading taken at any time beyond 5 min [*Figure 10(B)*] gives an estimate of the completeness of the activation.

CONCLUSION

This paper has summarized some observations and interpretations concerning the activation, acetylation and degradation reactions involved in the synthesis of cellulose acetate, and the complex roles that sulphuric acid plays in this system.

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