ON THE MECHANISM OF CELLULOSE ACETYLATION

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INTRODUCTION

The inability of acetic anhydride to acetylate pulp efficiently in the absence of a catalyst has received much attention from different research workers. In fact the acetylation with acetic anhydride is unsuccessful if pre-activation has not been carried out. It can be assumed that the energy of interaction between acetic anhydride and cellulose in the absence of a catalyst is insufficient to weaken the intermolecular action in cellulose.

Theoretical considerations as regards the process of acetylation indicate that the following procedures can be followed for effective acetylation.

1. The pulp is treated with reagents which cause a rupture or weakening of intermolecular bonds. In such a case, agents which give rise to swelling, or dissolution of the pulp, serve as "catalysts".

2. Substances which are capable of reacting with cellulose are added to the acetylation bath. The resulting intermediates have groups which are substituted for acetate groups during the reaction with acetic anhydride. The energy of at least one of the two reactions must be high enough to weaken the intermolecular action.

3. Substances which react with acetic anhydride are added to the acetylation bath. These form intermediates capable of reacting with cellulose. The energy of interaction of these intermediates with cellulose has to be of a magnitude such that the intermolecular action is weakened.

A large number of substances have been proposed as catalysts for acetylation. Of these, sulphuric and perchloric acids have found the most extensive application. The mechanism of the catalytic actions of sulphuric and perchloric acids in cellulose acetylation was studied by measuring the conductivity of acetylating mixtures with and without cellulose. A special device was used for recording the conductivity which changed with time. This device consisted of a sound generator, a registering potentiometer and a special arrangement.

STUDY OF ACETYLATING MIXTURES WITHOUT CELLULOSE

While preparing mixtures consisting of acetic anhydride, methylene chloride and sulphuric acid, the conductivity decreases because of the reaction between sulphuric acid and acetic anhydride with the formation of their compound (supposedly acetylsulphuric acid). The kinetics of this reaction is well described by the equation of the pseudo first order reaction. *Table 1* shows the rate constants of this reaction at different temperatures. The energy of activation of this reaction is calculated by means of these

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Table 1. Temperature influence on rate constants of the reaction proceeding in H_2SO_4 or $HClO_4$ solutions in 40 : 60 (% by vol.) mixture of acetic anhydride and methylene chloride

Temperature (°C)	$K \times 10^2$ min^{-1}	
	0·02 M H_2SO_4	0·005 M $HClO_4$
40	14·3	15·5
35	7·97	—
30	3·39	8·9
25	1·22	4·4
20	0·75	3·2
10	0·072	—

$E = 31\cdot2$ kcal/mole; $E = 14\cdot2$ kcal/mole
$K_0 = 10^{20\cdot5}$; $K_0 = 10^{9\cdot1}$

data. Addition of a small amount of acetic acid to the acetylating mixture considerably slows down the reaction which proceeds in the mixture.

Table 2 represents the rate constants of the reaction which proceeds in the acetylating mixture in presence of different amounts of acetic acid. These data show that the reaction practically does not proceed in acetic acid medium.

Table 2. Influence of acetic acid addition on rate constants of the reaction proceeding in sulphuric or perchloric acid solution in admixture with acetic anhydride and methylene chloride at 40°C

	Mixture composition (vol. %)			$K \times 10^2$ min^{-1}	
$(CH_3CO)_2O$	CH_2Cl_2	CH_3COOH		0·02 M H_2SO_4	0·005 M $HClO_4$
40	60	—		14·3	15·5
40	59	1		—	8·7
40	58	2		4·38	6·1
40	57	3		—	5·1
40	56	4		2·49	3·1
40	55	—		—	2·4
40	54	6		1·5	—
40	52	8		1·1	—
40	50	10		1·03	1·6
40	40	20		—	0·89

The interaction between acetic anhydride and perchloric acid proceeds in mixtures consisting of acetic anhydride, methylene chloride and perchloric acid (without cellulose). The result of this reaction is the formation of acetyl perchlorate. This interaction results in an increase in the conductivity of the mixture. The kinetics of this reaction may also be described formally by the equation of the reaction of the pseudo first order. Table 1 shows the rate constants of these reactions at different temperatures. Based on these data the energy of activation was calculated. Addition of acetic acid to the acetylating mixture in this case also slows down the reaction proceeding in this mixture. Table 2 shows the influence of acetic acid addition on the rate constants of the reaction in the mixture.

MECHANISM OF CATALYSIS WITH SULPHURIC ACID

Although the mechanism of catalysis with sulphuric acid has been the subject of considerable study, different investigators have arrived at rather contradictory results. Our investigations have shown that the mechanism of catalysis with sulphuric acid is dependent on the composition of the acetylation bath and on the reactivity of the pulp utilized.

The mechanism of acetylation with acetic anhydride in the acetic acid medium is mainly based on the formation of cellulose sulphate, resulting from the reaction of cellulose with sulphuric acid. The cellulose is *trans-*esterified from sulphate to acetate through a sulphoacetate intermediate stage. This mechanism of acetylation is independent of the reactivity of the pulp concerned.

Figure 1 shows the conductivity changes on acetylating different kinds of cellulose. The descending part of the curve corresponds to the beginning of the process when the reaction of the sulphate cellulose formation dominates.
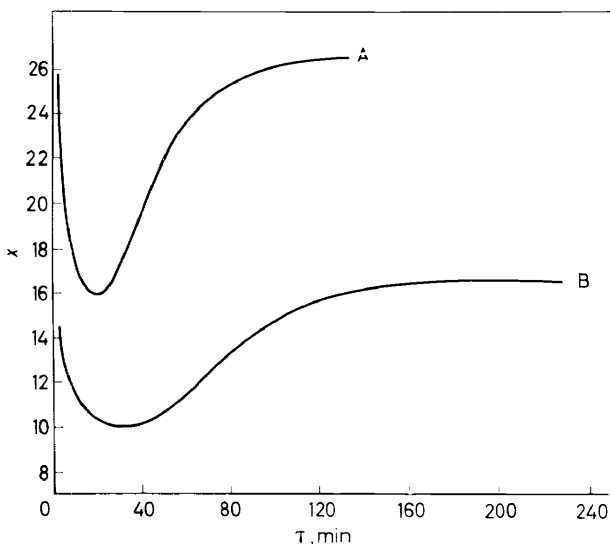

Figure 1. Conductivity changes on acetylating different kinds of cellulose

The horizontal part of the curve, or the minimum point of the curve as the limit corresponds to the dynamical equilibration between the sulphate cellulose formation and its re-esterification. The descending part of the curve corresponds to the main part of the acetylating process when the lessening of the coherent sulphuric acid content occurs. The rate constants of the sulphation and acetylation of the beginning and the main fraction of cellulose were determined on the basis of conductivity curves.

Upon acetylation with acetic anhydride when acetic acid is virtually absent (e.g. acetylation in methylene chloride), sulphuric acid reacts with acetic anhydride in the acetylation bath, with the formation of an intermediate [presumably acetylsulphuric acid (reaction 1)], as it was shown before.†

† Our considerations appear to be true if we assume, as L. Laamanen and H. Sihtola suggest, that monoacetylsulphuric acid and diacetylsulphuric acid are formed under these conditions.

When the substance formed reacts with cellulose, cellulose acetate is formed, and sulphuric acid set free (reaction 2). The sulphuric acid liberated can react once again, either with acetic anhydride (reaction 1), or with cellulose forming a sulphate. If the reactivity of the pulp is good, then the rate of reaction 2 is considerably higher than that of reaction 1. For this reason, the acetylation mixture contains mainly free sulphuric acid rather than acetylsulphuric acid. Under these conditions, acetylation proceeds primarily through cellulose sulphate.

If the reactivity of the pulp is poor, then the rate of reaction 2 is low, and below that of reaction 1. For this reason, the sulphuric acid occurs mainly as acetylsulphuric acid, and is not in the free state. Under these circumstances the acetylation mainly proceeds through acetylsulphuric acid.

Thus, when acetylating cellulose in methylene chloride medium the mechanism of acetylation changes according to the reactivity of the cellulose used. That is why the acetylation process in manufacturing is not stable. It depends on the reactivity of initial cellulose and the acetic acid content in the acetylating mixture. Due to this the time of acetylation practically varies widely. The process may be stabilized by addition of small amounts of acetic acid to the acetylating mixture. In this case the mechanism of acetylation will result in the formation of sulphate with the following re-esterification. It does not depend on the reactivity of cellulose.

The investigation showed that the acetylation through sulphates was more preferable than the acetylation through acetylsulphuric acid. So, acetylation (up to a clear solution) of well activated cellulose in presence of acetic acid lasted 4 h 15 min, and without acetic acid it lasted 5 h 30 min. The acetylation of badly activated cellulose in the presence of acetic acid lasted 6 h, and without acetic acid, 28 h. Therefore, addition of acetic acid to the acetylating mixture consisting of acetic anhydride, methylene chloride and sulphuric acid increases the reproductivity of the acetylation process and decreases the time of this reaction. It is so because the acetylation process in this case has a more preferable mechanism (through cellulose sulphate) and does not depend on the reactivity of the cellulose acetylated.

When the acetylation through cellulose sulphate proceeds, the rate of reaction depends mainly on the ratio between amounts of sulphuric acid and cellulose but not on the concentration of catalyst in solution.

MECHANISM OF CATALYSIS WITH PERCHLORIC ACID

A great deal of research has been devoted to the action of perchloric acid as a catalyst in the acetylation of cellulose. On the one hand it is proved that while interacting with acetic anhydride, perchloric acid forms acetylperchlorate which appears to be the acetylating agent. On the other hand, some indications show that perchloric acid can react with cellulose forming certain bonds. Thus, it gives rise to the problem of a more preferable mechanism of perchloric acid action. As mentioned above the reaction between perchloric acid and acetic anhydride can be controlled by taking into account electrical conductivity of acetylating mixtures.

Acetylperchlorate being considered as the main acetylating agent, the best results of acetylation must be received by using the "ageing" mixtures

in which the formation of acetylperchlorate has already taken place. On the other hand, if the second mechanism with perchloric acid acting as a catalyst is more preferable the best results will be obtained by using "fresh" mixtures. Comparative acetylation of cellulose by using "ageing" mixtures and "fresh" mixtures showed that the rate of acetylation by means of "fresh" mixtures is much more higher than that of acetylation by means of "ageing" mixtures. Thus, the acetylation by means of mixtures in which the reaction between acetic anhydride and catalysts has not taken place is also more preferable in the case when we use perchloric acid as a catalyst·

The rate of reaction in the presence of perchloric acid depends mainly on the concentration of the catalyst in solution.

MICROEXPRESS METHOD OF EVALUATING THE KINETICS OF CELLULOSE ACETYLATION

Since 1964 we, together with L. Perepechkin, have used the microexpress method of evaluating the kinetics of heterogeneous cellulose acetylation in order to solve a number of problems connected with kinetics and mechanisms of acetylation. The essence of this method is that acetylation proceeds in the gradient column, the acetylating agent and catalyst being a part of the flotation solution. The concentrations of the acetylating agent and the catalyst are constant in the vertical direction.

The gradient column has the gravity about 1·55 at its bottom and about 1·25 at the top. It is known that cellulose has a density of about 1·5 while the triacetate gives a value of 1·3. The change of acetate density is connected simply and almost linearly with its degree of substitution.
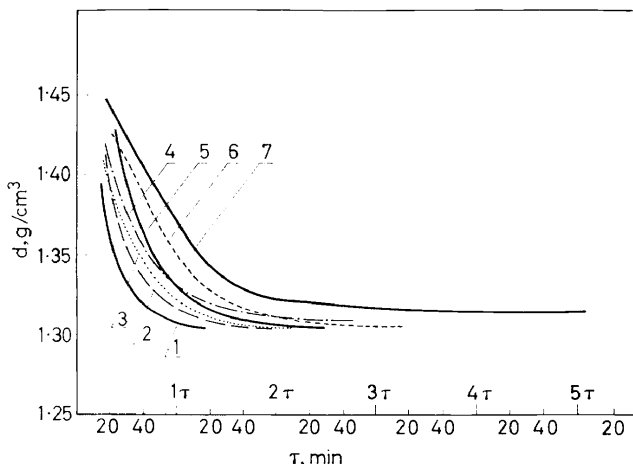

Figure 2. Evaluating the kinetics of acetylation for different kinds of cellulose [curves 1–7 correspond to the numbers 1–7 in *Table 3*]

In the course of acetylation the samples of cellulose move vertically and the control of the kinetics of acetylation comes to the control of the move-

ment of these samples. The acetylation of different kinds of cellulose are shown in *Figure 2*.

Table 3. The rate constants of acetylation samples of cellulose

No.	$K \times 10^2 \, \text{min}^{-1}$
1	7·06
2	5·39
3	4·55
4	3·25
5	3·07
6	3·11
7	0·93

As may be seen from *Figure 2* and *Table 3*, this method gives the opportunity of evaluating the kinetics of acetylation for different kinds of cellulose. Thanks to this simplicity it may be widely recommended both for industrial and research purposes.