DECOMPOSITION OF SULPHURIC ESTERS OF CELLULOSE FORMED DURING ACETYLATION OF CELLULOSE

A. DELSEMME

U.C.B. Division Fabelta, Tubize, Belgium

INTRODUCTION

Sulphuric acid is still the most frequently used catalyst in industrial acetylation processes of cellulose due to the efficiency and the low cost of this catalyst.

It has been known for a long time[1,2] that during acetylation, sulphuric acid combines with cellulose, forming acid sulphate groups. When the esterification is complete and in the presence of a small excess of anhydride, sulphuric acid remains quantitatively combined. Malm[2] reported that the combined acid is rapidly hydrolysed when the first steps of ripening of cellulose acetate take place. However, this hydrolysis never seems complete, even after several hours of ripening. In this way a consequent stabilizing step is needed for acetates prepared with great amounts of catalyst during esterification and ripened at low temperature. Acid sulphate groups reduce thermal stability and solubility of cellulose acetate, and are dependent on the concentration of catalyst in esterification.

All this suggests that the hydrolysis of combined sulphuric acid is limited by an equilibrium. The present work was designed to find the conditions of establishment of this equilibrium and the way to displace it, in order to improve the properties of the final product and to suppress the stabilizing step. As a prelude to this study and in order to simplify the system, the decomposition of non-neutralized cellulose sulphate has been analysed. It has been assumed that this reaction proceeds in the same way as that for acid sulphate groups of cellulose acetate.

## DECOMPOSITION OF NON-NEUTRALIZED CELLULOSE SULPHATE

Cellulose sulphate is readily prepared by a trans-esterification reaction between butyl sulphate and cellulose in concentrated sulphuric acid, according to the original patents[3]. Degrees of substitution comprised between 0·3 to 1 are easily achieved by working with different co-solvents.

Cellulose sulphate is soluble in water and fairly soluble in N,N-dimethylformamide (DMF), provided its molecular weight is not too high. Addition of small amounts of water to this solvent improves greatly the solubility of cellulose sulphate. Unfortunately this compound is insoluble in acetic acid. Water has been rejected as solvent because of the particular behaviour of the reaction in this medium, the reaction is very slow, no equilibrium has

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been observed, the activation energy is high (± 28 kcal) and seems to be dependent on temperature.

Dimethylformamide has thus been chosen as the reaction medium. The progress of the reaction can be easily followed by measuring the increase of acidity of the solution as a function of time; one gram H^+ ion is produced by the decomposition of one mole of sulphate. The reaction is carried out in sealed glass tubes (30 ml) placed in a thermostatic bath. At room temperature the solution is sufficiently stable for 2–3 h but it is kept in melting ice while all manipulations are taking place.

From the results obtained plots of concentration against time can be traced. Graphically rate–concentration plots can be derived from preceding ones. These last curves cut the concentration axis at a value x_e, which is the extent of the reaction when equilibrium is reached (*Figure 1*). The shape of rate–concentration curves is characteristic of the system of coupled reactions. In the present case, this shape is that of a system composed of a first order reaction limited by a second order one (*Figure 1*).
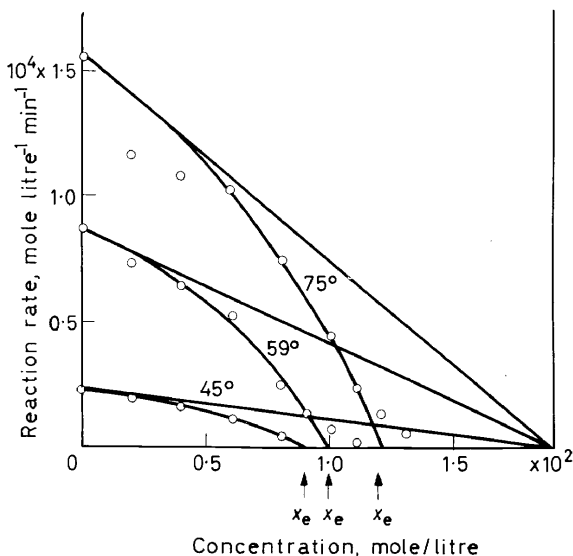
Figure 1. Variation of the rate of reaction with concentration at different temperatures

The expression for the rate of such a system is as follows:

$$V = \frac{\mathrm{d}x}{\mathrm{d}t} = k_1(a - x)\, b - k_2 x^2 \tag{1}$$

Where x represents the amount of sulphate decomposed at time t; a and b the initial concentrations of sulphate and water respectively and k_1 and k_2 the rate constants of the coupled reactions. Water concentration can be considered most of the time as a constant for normal moisture of sulphate and solvent provided it is greater than stoichiometric value.

From the equilibrium relation:

$$k_1(a - x_e)\, b = k_2 x_e^2 \tag{2}$$

the value of k_2 is expressed by equation (2) and substituted in equation (1) which gives after integration

$$k_1 t = \frac{x_e}{b\,(2a - x_e)} \left[\ln \frac{x_e}{x_e - x} - \ln \frac{\dfrac{a x_e}{a - x_e}}{\dfrac{a x_e}{a - x_e} + x} \right] = \phi(x) \qquad (3)$$

Equation (3) is the kinetic law of the system.

Applications of equation (3) are shown in *Figure 2*; they relate to a solution of 2×10^{-2} M/l. of sulphate with a water content almost twice the stoichiometric value.
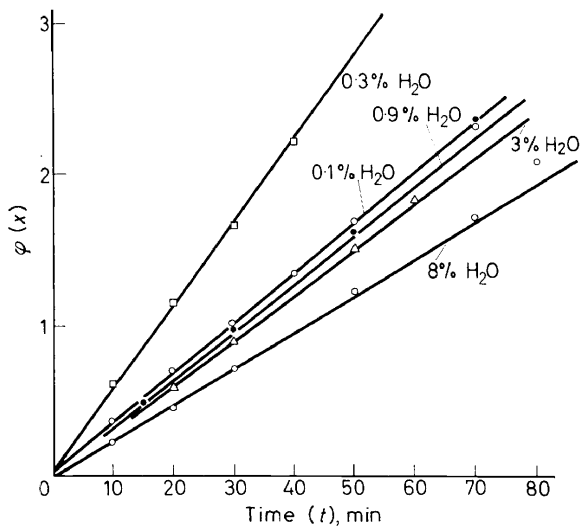
Figure 2. Decomposition of cellulose sulphate—application of equation (3); $kT = \psi(x)$
[Temperature: 45°C]

Table 1 (column 1) gives the rate constant values of the forward reaction obtained at different temperatures. Activation energy determined from these values is found to be 15 kcal. If water concentration is increased, the rate constant of forward reaction undergoes modifications but equation (3)

Table 1. Values of k_1 (M^{-1} sec^{-1})

T (°C)	Water in the solvent (%)					
	0·02	0·1	0·3	0·9	3	8
45	$1·68 \times 10^0$	$2·7 \times 10^{-1}$	$1·08 \times 10^{-1}$	$2·44 \times 10^{-2}$	$4·43 \times 10^{-3}$	$3·42 \times 10^{-4}$
59	$5·8 \times 10^0$	$1·09 \times 10^0$	$3·86 \times 10^{-1}$	$9·68 \times 10^{-2}$	$1·48 \times 10^{-2}$	$2·31 \times 10^{-3}$
75	$9·6 \times 10^0$	$3·24 \times 10^0$	$5·98 \times 10^{-1}$	$2·15 \times 10^{-1}$	$6·25 \times 10^{-2}$	—
E	15	18	13	16	19	28

remains valuable. *Table 1* indicates the values of k_1 for different water contents and temperatures. Values of activation energy in each set of conditions are also given in *Table 1* (last line).

Table 2 gives the corresponding values of x_e under the same experimental conditions as in *Table 1*.

Table 2. Values of x_e (% complete reaction)

T (°C)	Water in the solvent (%)					
	0·02	0·1	0·3	0·9	3	8
45	47	62	51	55	40	12
59	52·5	65	59	68	56	23
75	63	69	88	85	67	—

These results show first that the decomposition reaction of combined sulphuric acid is a limited reaction and secondly, that the rate and extent of forward reaction depends on the water content of the medium; the highest rate being obtained with smaller water contents. This last dependence is normal because the reaction is proton-controlled. A correlation with the acidity function of the solution would probably confirm this view.

APPLICATION TO CELLULOSE ACETATE

In order to apply these results to cellulose acetate let us consider a definite case. To an acetic dope of cellulose triacetate† (after acetylation and before ripening) containing $9·8–10^{-1}$ moles/l. of combined sulphuric acid (x) and a small excess of acetic anhydride (no CH_2Cl_2) water is added to reach a concentration of 0·3 moles/l. (about 0·5 per cent based on the dope).
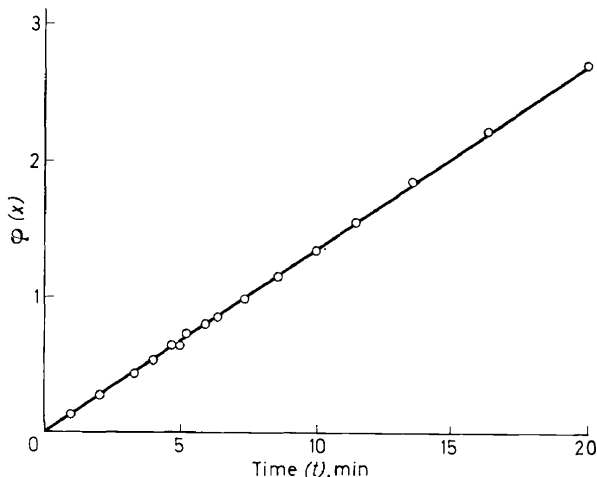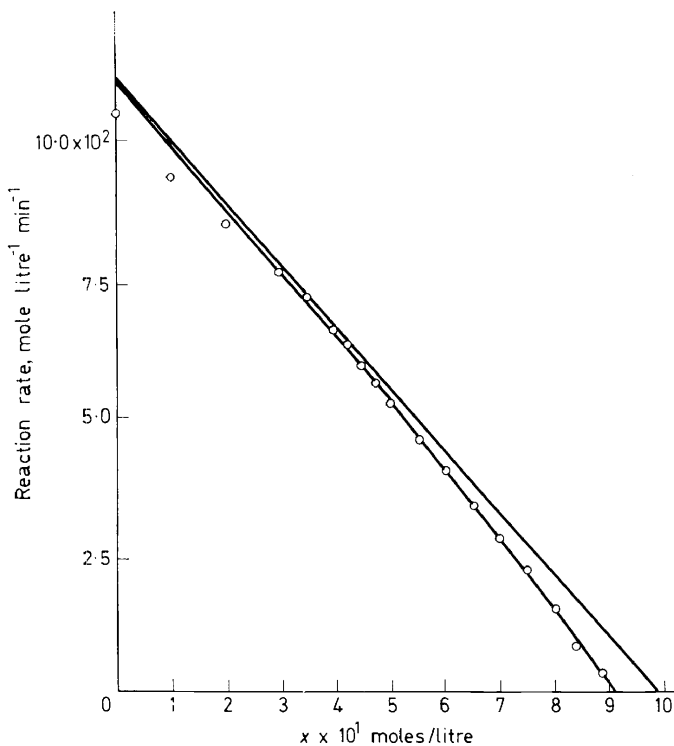

Figure 3. Desulphation of cellulose acetate—rate–concentration curves

† This acetate was obtained by an acetylation employing 14 per cent catalyst (based on cellulose).

Samples are neutralized after different periods of reaction at 30°C.

Application of equation (3) to the results is given in *Figure 3*. The correlation is good. Rate constant k_1 of forward reaction is determined as $4 \cdot 1 \times 10^{-1}$ ($M^{-1} sec^{-1}$) at 30°C and x_e is found to be equal to 94 per cent (*Figure 4*). Activation energy measured at different temperatures is 23·5 kcal.

Figure 4. Desulphation of cellulose acetate—application of equation (3) [Temperature: 30°C]

An experiment has been carried out to measure the effect of water content of the solvent. All the samples but one were too unstable to be measured. From this, we can conclude that the water concentration corresponding to this stable sample was really near the optimum value; it was similar to the value found for cellulose sulphate. These results confirm the applicability of the kinetic law established with cellulose sulphate for acetate.

DISPLACEMENT OF EQUILIBRIUM

In order to displace the former equilibrium and, then, to improve the stability of cellulose acetate two ways have been followed. (1) By neutralizing the maximum fraction of free sulphuric acid without the combined acid being neutralized; (2) By increasing temperature—the reverse reaction being probably exothermic.

Table 3 gives the results obtained by a combination of the two variables in the same experiment. Four different extents of neutralization were achieved at three different temperatures. Samples were precipitated after 17 h of reaction. By this time equilibrium had been reached.

Results are expressed in two manners: (1) by $a - x_e$, extent of the forward reaction at equilibrium expressed in mg per cent combined sulphuric acid; and (2) by decomposition temperature when the amount of combined acid is below the level of sensitivity of the potentiometric titration method[5]. This temperature was considered to give the best indication available in this case. The determination of total sulphur of the compounds, according to Malm[6] is more difficult in this case with regard to the relatively high content of the samples in neutral sulphate groups.

Table 3. Values of $a - x_e$ and decomposition temperatures at equilibrium

T (°C)	Extent of neutralization of total catalyst							
	50%		65%		85%		95%	
	$a - x_e$	T dec	$a - x_e$	T dec	$a - x_e$	T dec	$a - x_e$	T dec
25°	53·9	—·	32·1	—	17·8	235	239	183
40°	11·8	276	4·2	—	2·3	272	191	184
55°	<2	273	<2	276	<2	284	<2	272

Values of $a - x_e$ are expressed in mg per cent acetate.

Table 3 shows that action must be brought on the two above mentioned variables at the same time, to reach a stable triacetate. The extent of neutralization must correspond the most accurately to the free acid quantity and must not exceed beyond this limit, because combined acid will be neutralized and definitively blocked; this occurred when 95 per cent of the total had been neutralized (*Table 3*; last column). Neutralization alone or temperature are not sufficient to reach the stability wanted. The combination of these two variables leads to expected results. It is necessary to specify that viscosity and acetyl content of cellulose triacetate are practically unaffected by the upper treatment.

CONCLUSIONS

The kinetic study of desulphation of cellulose acetate after acetylation has lead to fitting the reaction conditions in such a way as to displace the equilibrium limiting this reaction. This has enabled preparation of cellulose acetate of improved stability at laboratory and pilot plant scales. By other ways such an acetate would have required a further stabilizing treatment.

The purpose has been reached by (1) setting the water content of the solvent at a minimum value in order to assure a rapid desulphation reaction; (2) by neutralizing afterwards most of free sulphuric acid but with fitting the extent of neutralization to the amount of free acid present in the mixture; and (3) by raising temperature almost to 50–55°C. Such

conditions can be found for any process even for the ones that employ small amounts of sulphuric acid.

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