

# Kinetics of acid catalysed degradation of cellulose triacetate in chloroalkane solvents:

## 1. Dichloromethane

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The kinetics of degradation of cellulose triacetate in a dichloromethane–acetic anhydride mixture with perchloric or sulphuric acid catalyst was studied. Decrease in molecular weight with time was followed viscometrically using limiting viscosity numbers, calculated by a single-point method, and Mark–Houwink constants for the solvent mixture. Dependence of first-order rate constants on catalyst concentration and temperature was investigated and Arrhenius parameters, activation entropies and catalytic coefficients were obtained. A suggested reaction mechanism for degradation based on  $H^+$  and  $Ac^+$  (acetylum ion) acting as catalytic species is proposed.

(Keywords: kinetics; degradation; cellulose triacetate; acid catalysis)

### INTRODUCTION

The preparation of cellulose acetate from cotton linters using either a sulphuric or perchloric acid catalyst, in the presence of acetic anhydride, inevitably gives a product of lower molecular weight due to chain scission. Since the catalyst clearly has a dual role by acting in both the acylation and degradation processes, the overall catalytic mechanism is complex and presently not fully understood. Both processes are also obscured by the heterogeneous nature of the acylation conditions, particularly in the earlier stages. A useful way of investigating the degradative process under controlled homogeneous conditions, in the absence of simultaneous acetylation, is to measure degradation rate constants for cellulose triacetate dissolved in acetic anhydride–solvent mixtures.

This approach was made in an earlier paper<sup>1</sup> for the cellulose triacetate–acetic anhydride–chloroform system where previous literature is reviewed. Since then no relevant work has appeared in the literature and the present paper now extends this study. Dichloromethane solvent is of particular interest in view of its use in the manufacture of cellulose triacetate.

### EXPERIMENTAL

#### *Materials*

Cellulose triacetate (CTA) was prepared by the heterogeneous acetylation of purified cotton linters at 70°C in a carbon tetrachloride–acetic acid–acetic anhydride (freshly distilled and dried)–zinc chloride mixture whose respective weights were 63.6, 1.57, 10.9 and 0.20 g per gram of cotton. The fibrous product obtained was washed successively with petroleum ether, absolute alcohol and finally distilled water before vacuum oven drying for 4 h at 110°C. Various samples within the molecular weight range  $(30–100) \times 10^3$  could be prepared by altering the reaction time (5–8 days). Saponification analysis<sup>2</sup> of the

products gave an acetic acid yield of at least 62.3% in each case, compared with the theoretical value of 62.49% for cellulose triacetate. Full acetylation was also confirmed by semi-micro combustion analysis of selected samples.

Both sulphuric and perchloric acid (72% w/w) used as degradation catalysts were B.D.H. Analar quality and the exact perchloric acid concentration was determined by titration. Acetic anhydride for degradation studies was purified<sup>3</sup> before use and stored over a molecular sieve; because of its extremely hygroscopic nature it was redistilled every two weeks. Dichloromethane (methylene chloride) was purified<sup>4</sup> and stored over a molecular sieve before use. All solution concentrations were made up using Grade A volumetric glassware throughout the degradation studies.

#### *Degradation runs*

A weighed amount of vacuum dried CTA was dissolved in dichloromethane to give a 250 ml stock solution and kept at the working temperature at least three days before use. The catalyst was weighed into a volumetric flask, in a dry-box, to give a 25 ml stock solution in a weighed amount of acetic anhydride. A measured volume was then added to a second volumetric flask, a little dichloromethane was added and the stoppered flask brought to temperature in the thermostat. A measured quantity of thermostatically controlled CTA stock solution was transferred to this flask and the solution immediately made up to the mark with thermostatically controlled solvent. After shaking, to ensure complete mixing, about 10 ml was filtered (No. 3 sinter) into an Ubbelohde suspended-level viscometer in the thermostat.

The zero-time for commencement of degradation was taken as that at which the CTA solution was added to the catalyst solution. Viscometer flow-times for the solution, measured by stopwatch ( $\pm 0.01$  s), were recorded at time intervals extending over 150 min. A specially designed

head, comprising PTFE taps, connected the viscometer with solvent traps and drying tubes to prevent solution evaporation and atmospheric moisture contamination during the degradation runs.

Limiting viscosity numbers (LVN), obtained from the flow-times, were used to calculate the molecular weight of CTA at each degradation reaction time as described below. Solvent flow-times were measured for the same dichloromethane-acetic anhydride composition (without catalyst) at each working temperature.

All degradation runs were carried out with a CTA concentration of  $0.800 \text{ g dl}^{-1}$  and an acetic anhydride concentration of  $2.12 \text{ mol dm}^{-3}$ .

#### Determination of LVN

These were calculated from viscosity numbers ( $\eta_{sp}/c$ ) measured at each reaction time using the single-point viscosity equation of Solomon and Gotesman<sup>5</sup>. This relationship was chosen for its simplicity of application and gave the LVN correct to 2–3% over the range of temperatures studied.

#### Molecular weight at each reaction time

This was obtained from the calculated LVN using the K and  $\alpha$  Mark-Houwink constants previously determined for CTA in the solvent mixture at each of the working temperatures. Prepared CTA samples with osmometrically determined (Hewlett-Packard Model 502 membrane osmometer)  $\bar{M}_n$  values of 38914, 54378 and 72805 were used for this. K and  $\alpha$  values were in the range  $(1.5\text{--}5.0) \times 10^{-5} \text{ dl g}^{-1}$  and 0.91–1.04, respectively, and the estimated uncertainty in  $\bar{M}_n$  calculated in this way was about 2%.

## RESULTS

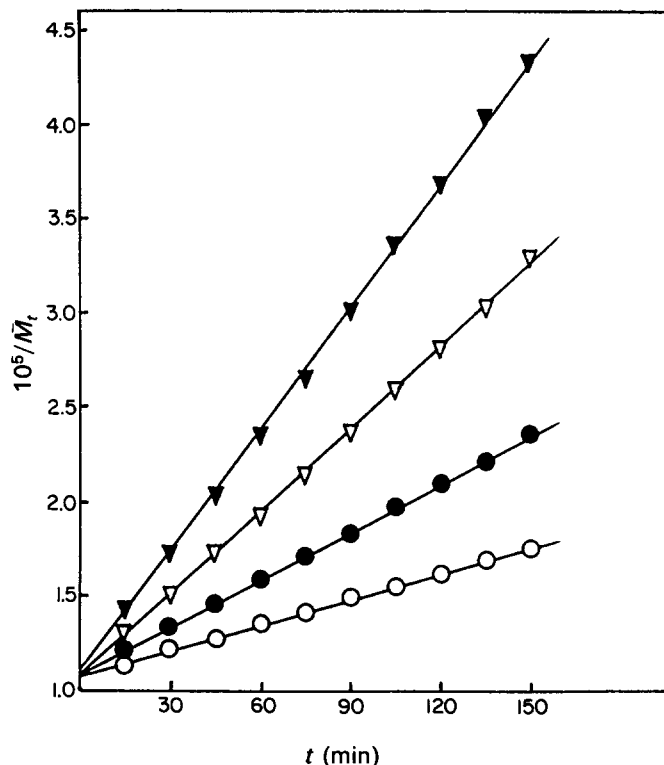
#### Treatment of kinetic data

This was based on the theoretical approach to a random degradation process made earlier by Kuhn<sup>6</sup> and more recently discussed by Grassie<sup>7</sup>. We make the assumption that each oxygen link between glucopyranose units of cellulose triacetate is equally susceptible to scission, in which case the first-order kinetic equation is:

$$\frac{1}{\bar{M}_t} = \frac{1}{\bar{M}_0} + \frac{kt}{288.2} \quad (1)$$

where  $\bar{M}_t$  and  $\bar{M}_0$  are the number-average molecular weights after time  $t$  and at the start of the reaction ( $t=0$ ), respectively. The rate constant,  $k$ , represents the fraction of  $\text{--O--}$  links between monomeric glucopyranose units broken in unit time and 288.2 is the mass of a glucopyranose triacetate unit. In the present work rate constants were obtained from slopes of the linear plots of  $10^5/\bar{M}_t$  against  $t$  or, where curvature was observed, from the initial slope at zero time as described later. Kinetic plots should have a common intercept value of  $10^5/\bar{M}_0$  (equation (1)) and slope equal to  $10^5 k/288.2$ .

The effect of temperature on rate of degradation was treated in terms of the Arrhenius equation and the pre-exponential factor ( $A$ ) and activation energy ( $E_a$ ) were evaluated from convenient linear  $\log k$  versus  $1/T$  plots in the usual way. The pre-exponential factor was assumed to be independent of temperature in these studies.



**Figure 1** Kinetic plots for perchloric acid catalysed degradation of CTA in dichloromethane ( $2.12 \text{ mol dm}^{-3} \text{ Ac}_2\text{O}$ ) at  $18^\circ\text{C}$ . Values given  $\times 10^{-3} \text{ mol dm}^{-3} \text{ HClO}_4$  (○) 1.65; (●) 3.30; (△) 5.40; (▲) 7.20

#### Degradation with perchloric and sulphuric acid catalysts

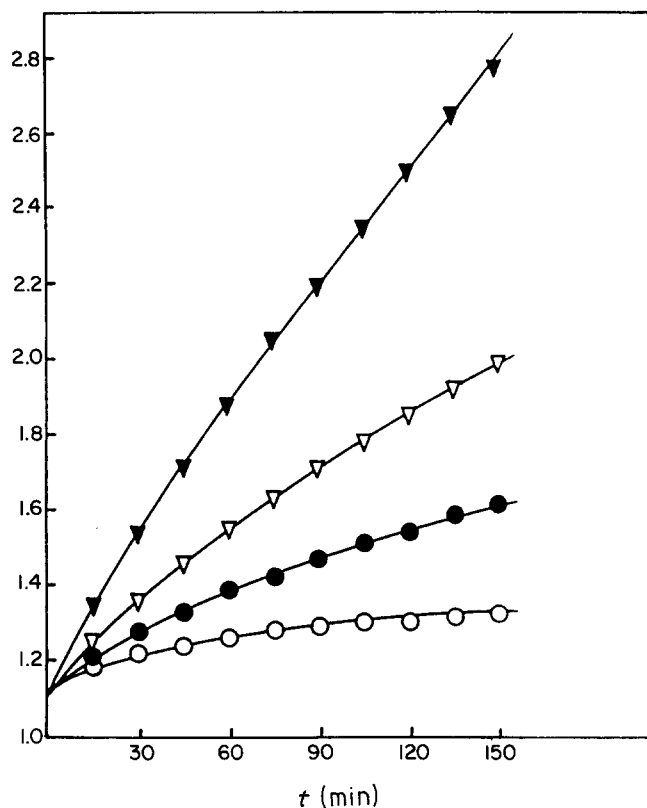
Typical kinetic plots for perchloric and sulphuric acid concentrations  $(1.65\text{--}7.20) \times 10^{-3}$  and  $(2.00\text{--}6.00) \times 10^{-2} \text{ mol dm}^{-3}$ , respectively, at  $18^\circ\text{C}$  are shown in Figures 1 and 2.

A CTA sample having  $\bar{M}_n = 91140$  was used throughout the degradation studies in dichloromethane. Where linear plots were obtained their slopes were evaluated in the usual way by the method of least squares. For curved plots (discussed later) the rate constant was calculated from the initial slope at  $t=0$  for the 'best-fit' polynomial equation obtained by least squares regression analysis. The choice of polynomial order for 'best fit' was based on the lowest standard deviation between calculated and experimental points consistent with closest agreement with the theoretical intercept value. For all kinetic plots the mean difference between experimental and theoretical intercept values was 6%.

The variation of rate constant with catalyst concentration and temperature is shown in Table 1. No degradation of CTA was observed in the absence of catalyst.

Earlier work<sup>1</sup> suggested a possible linear relationship between rate constant and low catalyst concentrations, and the plots of rate constant against catalyst concentration were examined. If, for temperatures up to  $25^\circ\text{C}$ , these are assumed to be linear for perchloric and sulphuric concentrations up to  $7.2 \times 10^{-3}$  and  $4.0 \times 10^{-2} \text{ mol dm}^{-3}$ , respectively, then the relevant catalytic coefficients ( $10^{-3} \text{ min}^{-1}/\text{mol dm}^{-3}$ ) at  $15^\circ\text{C}$  are 6.07 ( $\text{HClO}_4$ ) and 0.485 ( $\text{H}_2\text{SO}_4$ ) compared to 17.7 ( $\text{HClO}_4$ ) and 1.14 ( $\text{H}_2\text{SO}_4$ ) at  $25^\circ\text{C}$ . Outside these limits direct proportionality between rate constant and catalyst concentration does not exist.

The applicability of the Arrhenius equation to the



**Figure 2** Kinetic plots for sulphuric acid catalysed degradation of CTA in dichloromethane ( $2.12 \text{ mol dm}^{-3} \text{ Ac}_2\text{O}$ ) at  $18^\circ\text{C}$ . Values  $\times 10^{-2} \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ : (○) 2.00; (●) 3.00; (▽) 4.00; (▼) 6.00

kinetic data (Table 1) was investigated for each catalyst concentration. Good Arrhenius plots were obtained and used to calculate the  $E_a$  and  $A$  values shown in Table 2. As a help in understanding the reaction mechanism the entropy of activation ( $\Delta S^\ddagger$ ) was calculated from the relationship<sup>8</sup>:

$$k = \frac{RT}{Nh} \exp \frac{\Delta S^\ddagger}{R} \exp -\frac{E_a}{RT} \quad (2)$$

where  $k$  is in  $\text{s}^{-1}$ ,  $N$  is Avogadro's number, and  $h$  is Planck's constant. Here  $E_a$  replaces the enthalpy of activation ( $\Delta H^\ddagger$ ) since the difference between these two quantities is negligible for solutions. Values for  $\Delta S^\ddagger$  at  $25^\circ\text{C}$  for both acid catalysts are shown in Table 2.

## DISCUSSION

### General considerations

The essentially linear kinetic plots for the perchloric acid catalysed degradation at  $15^\circ$  and  $18^\circ\text{C}$  (Figure 1) support the proposed first-order rate equation (equation (1)), although slight curvature was observed at higher temperatures. While some evaporation of solvent (b.p.  $40^\circ\text{C}$ ) during the reaction time would contribute to this, it is believed that the primary cause is a slow secondary side-reaction between catalyst and acetic anhydride resulting in a decrease in perchloric acid concentration with time; this effect for perchloric acid was not observed in previous work with chloroform solutions<sup>1</sup>. Evaluation of initial rate constants ( $t=0$ ) in such cases would seem to be the

**Table 1** Rate constants for perchloric and sulphuric acid catalysed degradation of CTA in dichloromethane (CTA concn.  $0.800 \text{ g dl}^{-1}$ ;  $[\text{Ac}_2\text{O}] = 2.12 \text{ mol dm}^{-3}$ )

	$10^5 k/\text{min}^{-1}$			
	$15^\circ\text{C}$	$18^\circ\text{C}$	$25^\circ\text{C}$	$30^\circ\text{C}$
$[\text{HClO}_4]/10^{-3} \text{ mol dm}^{-3}$				
1.65	0.827	1.31	2.86	4.22
3.30	1.80	2.43	5.76	8.55
5.40	3.38	3.88	9.68	14.9
7.20	4.42	4.98	12.68	23.1
$[\text{H}_2\text{SO}_4]/10^{-2} \text{ mol dm}^{-3}$				
2.00	0.970	1.17	2.26	3.16
3.00	1.41	1.75	3.42	4.82
4.00	1.98	2.37	4.59	6.87
6.00	3.08	3.87	7.23	10.7

**Table 2** Arrhenius parameters and entropies of activation for perchloric and sulphuric acid catalysed degradation of CTA in dichloromethane (CTA concn.  $0.800 \text{ g dl}^{-1}$ ;  $[\text{Ac}_2\text{O}] = 2.12 \text{ mol dm}^{-3}$ )

	$A/10^6 \text{ min}^{-1}$	$E_a/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{JK}^{-1} \text{ mol}^{-1}$ at $25^\circ\text{C}$
$[\text{HClO}_4]/10^{-3} \text{ mol dm}^{-3}$			
1.65	258	78.6	-103
3.30	2070	77.6	-101
5.40	2140	76.3	-100
7.20	57300	83.7	-73.0
$[\text{H}_2\text{SO}_4]/10^{-2} \text{ mol dm}^{-3}$			
2.00	0.532	59.3	-169
3.00	1.72	61.2	-160
4.00	3.15	61.9	-155
6.00	3.57	61.1	-154

best approach for both catalysts, and the smooth dependence of rate constant on concentration together with the satisfactory Arrhenius plots observed indeed supports this. Non-linear plots observed for all cases of sulphuric acid catalysed degradation have been previously reported in chloroform solutions by Bhatti and Howard<sup>1</sup>. These workers presented evidence in support of side-reactions between sulphuric acid and acetic anhydride, and such interaction is proposed here to explain the results in dichloromethane. The temperature dependence of the side-reactions accounts for the greater curvature of the plots observed at higher temperatures for these catalysts, although the nature of the side-reaction involving perchloric acid is at present unknown.

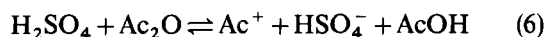
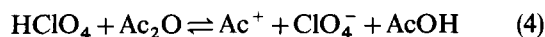
Perchloric acid is a very much faster catalyst than sulphuric, comparable rates of degradation being observed with perchloric acid concentrations about one tenth of those for sulphuric acid (Table 1). A similar difference in catalytic abilities for these acids has been reported for CTA in chloroform<sup>1</sup>, but in this solvent rate constants were 2–4 times those reported here for dichloromethane (Table 1).

The results in Table 2 show the energy of activation to be independent of catalyst concentration for both acids, as in ordinary catalysed reactions. Ignoring the high  $E_a$  value for  $7.20 \times 10^{-3} \text{ mol dm}^{-3} \text{ HClO}_4$ , the mean values for  $E_a$  in the case of perchloric and sulphuric acids are 77.5 and 60.9  $\text{kJ mol}^{-1}$  respectively. These are comparable to  $E_a$  for the acid catalysed hydrolysis of esters, and are close to the values previously reported for CTA degradation in chloroform<sup>1</sup>.

#### Reaction mechanism

Scission of the CTA chain under anhydrous conditions in the presence of acetic anhydride is believed to occur by acetolysis involving the acetic anhydride, the reaction mechanism having been discussed earlier<sup>1</sup>. Although the rate determining step would then be a bimolecular one between a linking oxygen atom and an acetic anhydride molecule, first order kinetics are observed (equation (1)) because the acetic anhydride concentration greatly exceeds that of the  $-\text{O}-$  linkages present ( $\sim 76$  times).

The mechanism previously proposed<sup>1</sup> can also be applied in the present case with the following relevant equilibria being set up:



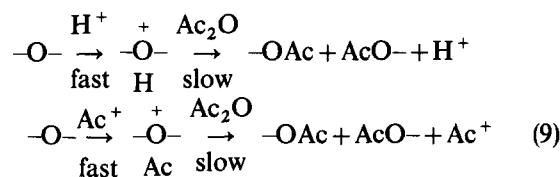
The effective catalytic species are suggested to be  $\text{H}^+$  and  $\text{Ac}^+$  (acetylium ion  $\text{CH}_3\text{CO}^+$ ). Thus the rate constant depends on the equilibrium concentrations  $[\text{H}^+]$  and

$[\text{Ac}^+]$  and their respective catalytic coefficients  $k_{\text{H}^+}$  and  $k_{\text{Ac}^+}$  as shown by:

$$k = k_{\text{H}^+}[\text{H}^+] + k_{\text{Ac}^+}[\text{Ac}^+] \quad (7)$$

While equilibria (3)–(6) are assumed to be rapidly established, the relative concentrations  $[\text{H}^+]$  and  $[\text{Ac}^+]$  would depend on the extent of these reactions, as determined by their respective equilibrium constants. A reaction mechanism based on these equilibria not only explains the difference in catalytic ability for the two acids, but also accounts for the dependence of rate constant on catalyst concentration. The much higher effective catalytic coefficients for  $\text{HClO}_4$  at 15° and 25°C, reported above, can be ascribed to markedly higher equilibrium constants for reactions (3) and (4) compared to equilibria (5) and (6) for  $\text{H}_2\text{SO}_4$ . The precise relationship between rate constant ( $k$ ) and total acid concentration in the case of each catalyst (see Table 1) clearly depends on the magnitude of these equilibrium constants, their temperature dependence, and the relative values of the catalytic coefficients  $k_{\text{H}^+}$  and  $k_{\text{Ac}^+}$  (equation (7)). It seems reasonable to assume that  $k_{\text{H}^+} > k_{\text{Ac}^+}$  and this might be a contributing factor to the greater increase in rate constant observed with higher catalyst concentrations.

The chain breaking process is believed to take place by means of the following reactions:



with the reaction between acetic anhydride and the charged intermediate complex being the rate determining step. Values of the Arrhenius parameters, together with the relatively large negative entropies of activation found (Table 2), are certainly consistent with a two-stage solvolytic process of this kind<sup>8</sup>. In equations (3), (5) and (8)  $\text{H}^+$  is written instead of its strictly solvated form  $\text{AcOH}_2^+$  since the former is believed to be the effective catalytic species.

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