Kinetics of acid catalysed degradation of cellulose triacetate in chloroalkane solvents:
2. Tetrachloroethane

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The kinetics of degradation of cellulose triacetate in a tetrachloroethane–acetic anhydride mixture with perchloric or sulphuric acid catalyst has been 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 was investigated and Arrhenius parameters, activation entropies and catalytic coefficients were obtained. A degradation reaction mechanism based on H^+ and Ac^+ (acetylium ion) as catalytic species is proposed.

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

INTRODUCTION

The relevance of cellulose triacetate degradation studies to the dual role of acid catalysts in the acetylation of cellulose has been discussed earlier[1,2]. In the so-called 'homogeneous acetylation' method the final product, cellulose triacetate, dissolves in the acetylation solvent such as chloroform, dichloromethane or tetrachloroethane in which cellulose trizcetate is readily soluble. Since the same catalytic species are believed to be involved for both acetylation and degradation[3], the dependence of acetylation rate on both nature of catalyst and solvent may be expected to parallel that shown in degradation rate studies. The present work enables kinetic degradation parameters to be compared for the above three chloroalkane solvents using perchloric and sulphuric acid catalysts.

EXPERIMENTAL

Materials

Preparation and analysis of cellulose triacetate (CTA) with AcOH yield $\nless 62.3\%$ (theoretical 62.49 wt%), characterization of the sulphuric and perchloric acid catalysts used, and purification of acetic anhydride have been described earlier[2]. The tetrachloroethane (1,1,2,2-tetrachloroethane) was purified[4] and stored over a molecular sieve (BDH Type 5A) before use. All solutions were made up in Grade A volumetric glassware throughout the degradation studies.

Degradation runs

A weighed amount of vacuum dried CTA was dissolved in the tetrachloroethane to give a 250 ml stock solution and kept at the working temperature at least three days before use. The acid catalyst was weighed into a volumetric flask in a dry-box to give a 25 ml stock solution containing a known weight of acetic anhydride. A measured volume was then added to a second volumetric flask, a little tetrachloroethane added and the stoppered flask brought to temperature in the thermostat. A measured quantity of CTA stock solution, at the same temperature, was transferred to the flask and the solution immediately made up to the mark with solvent at the same temperature. 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 degradation runs was taken as that at which the CTA stock solution was added to the catalyst solution. Viscometer flow-times for the solution, measured by stop-watch (± 0.01 s), were recorded at time intervals extending over 150 min. Solution evaporation and atmospheric moisture contamination during runs were prevented as described earlier[2].

The number-average molecular weight of CTA at each degradation reaction time was evaluated as follows. The limiting viscosity number, $[\eta]$, for a single flow time was obtained using a single-point viscosity equation[2]. Molecular weights were then calculated via the Mark–Houwink equation with appropriate constants evaluated (at each working temperature) using CTA samples of known number-average molecular weights as described earlier[2]. In the case of tetrachloroethane the Mark–Houwink constants were in the ranges $(1.8–2.8) \times 10^{-4}$ dl g^{-1} and 0.76–0.79 for K and α, respectively, and the average uncertainty in $\bar{M}_n$ calculated in this way, when compared with osmometric values, was 1.7%.

RESULTS

Treatment of kinetic data

The first-order kinetic equation used[2] for the degradation of CTA is given by:

$$\frac{1}{\bar{M}_t} = \frac{1}{\bar{M}_0} + \frac{kt}{288.2} \tag{1}$$

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 ether links between monomeric glucopyranose units

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broken in unit time and 288.2 is the mass of a glucopyranose triacetate unit. Rate constants were evaluated 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 reaction time[2]. Ideally the kinetic plots should have a common intercept value of $10^5/\bar{M}_0$ and slope of $10^5k/288.2$.

Variation of rate constant with temperature was treated in terms of the Arrhenius equation and the pre-exponential factor (A) and activation energy E_a evaluated as before[2].

Degradation with perchloric and sulphuric acid catalysts

Degradation runs were carried out with a CTA concentration of 0.800 g dl^{-1} and an acetic anhydride concentration of 2.12 mol dm^{-3}. The $\bar{M}_n$ values of CTA samples used for degradation runs at the indicated temperatures were 112035 (20°C), 99651 (25 and 30°C), 99802 (40°C) and 92607 (45°C). Satisfactory runs using sulphuric acid catalyst could not be obtained above 40°C due to the much faster side reaction between catalyst and acetic anhydride mentioned earlier[2]. However, satisfactory kinetic runs were obtained for perchloric acid up to 45°C.

Typical kinetic plots for perchloric acid concentrations up to 7.20×10^{-3} mol dm^{-3} at 20 and 25°C and sulphuric acid concentrations up to 6.00×10^{-2} mol dm^{-3} at 40°C are shown in *Figures 1* and *2*, respectively. For all the kinetic plots the mean difference between experimental and theoretical intercept values (equation 1) was 19%, which may be attributed to the more rapid catalyst side-reaction in tetrachloroethane compared with dichloromethane[2].

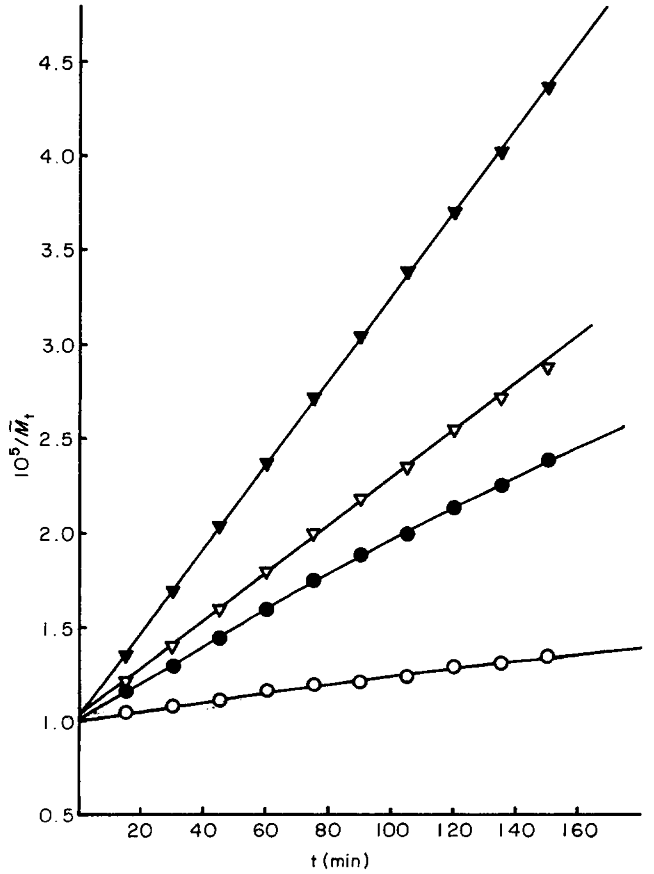


Figure 1 Kinetic plots for perchloric acid catalysed degradation of CTA in tetrachloroethane (Ac_2O 2.12 mol dm^{-3}). Values of $HClO_4$ given (mol dm^{-3}) at 20°C: ▽, 5.40×10^{-3}; ▼, 7.20×10^{-3}; and 25°C: ○, 1.65×10^{-3}; ●, 3.30×10^{-3}

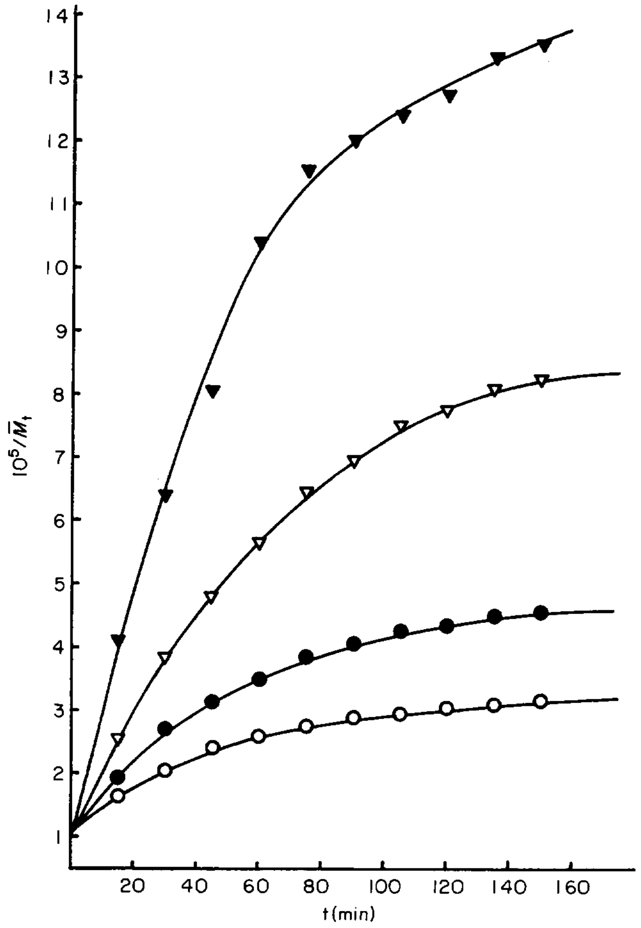


Figure 2 Kinetic plots for sulphuric acid catalysed degradation of CTA in tetrachloroethane (Ac_2O 2.12 mol dm^{-3}) at 40°C. Values of H_2SO_4 given (mol dm^{-3}): ○, 2.00×10^{-2}; ●, 3.00×10^{-2}; ▽, 4.00×10^{-2}; ▼, 6.00×10^{-2}

Table 1 Rate constants for perchloric and sulphuric acid catalysed degradation of CTA in tetrachloroethane (CTA concn 0.800 g dl^{-1}; $[Ac_2O] = 2.12$ mol dm^{-3})

$[HClO_4] \times 10^3$ (mol dm^{-3})	$k \times 10^5$ (min^{-1})				
	20°C	25°C	30°C	40°C	45°C
1.65	0.405[a]	0.732	1.26[a]	3.33	6.40
3.30	1.63[a]	3.04	5.68[a]	19.6	30.4
5.40	3.99	7.45[a]	14.0	41.0	64.7
7.20	6.38	11.63[a]	21.1	64.7	110.1
$[H_2SO_4] \times 10^2$ (mol dm^{-3})					
2.00	1.09	1.94	3.91[a]	13.9	24.5[a]
3.00	2.10	3.89	6.75[a]	19.9	33,4[a]
4.00	2.86	5.20[a]	9.24	29.4	49.5[a]
6.00	6.09	11.53	21.30[a]	69.4	120.6[a]

[a] Calculated from relevant Arrhenius equation

Rate constants for perchloric acid and sulphuric acid catalysed degradation of CTA for various catalyst concentrations and temperatures are shown in *Table 1*. Where necessary, additional rate constants were evaluated from Arrhenius parameters to facilitate direct comparison with previous rates in chloroform[1] and dichloromethane[2]; this also provided reliable rate constants for sulphuric acid at 45°C. No degradation of

Table 2 Arrhenius parameters and entropies of activation for perchloric and sulphuric acid catalysed degradation of CTA in tetrachloroethane (CTA concn 0.800 g dl^{-1}; $[Ac_2O] = 2.12$ mol dm^{-3})

$[HClO_4] \times 10^3$ (mol dm^{-3})	$A \times 10^{-8}$ (min^{-1})	E_a (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1}mol^{-1}) at 25°C
1.65	33.17	83.7	−96.6
3.30	4119	92.1	−56.7
5.40	1166	86.7	−67.1
7.20	3585	88.4	−57.8
$[H_2SO_4] \times 10^2$ (mol dm^{-3})			
2.00	32040	98.2	−40.0
3.00	370	85.6	−76.5
4.00	1975	88.9	−62.7
6.00	20150	92.7	−43.4

CTA in tetrachloroethane was observed in the absence of catalyst.

The linear dependence of rate constant on catalyst concentration at lower concentrations and temperatures reported earlier for dichloromethane[2] was not found for tetrachloroethane. For comparative purposes catalytic coefficients (10^{-3} min^{-1}/mol dm^{-3}) evaluated using lowest reported catalyst concentrations (*Table 1*) at 20°C are 2.45 ($HClO_4$) and 0.545 (H_2SO_4) compared with 4.44 ($HClO_4$) and 0.970 (H_2SO_4) at 25°C.

Good Arrhenius plots were obtained for both perchloric and sulphuric acid catalysed degradation. Energies of activation (E_a), pre-exponential factors (A), and entropies of activation ($\Delta S^{\ddagger}$) evaluated as described earlier[2] are shown in *Table 2*.

DISCUSSION

General considerations

The satisfactory linear kinetic plots for perchloric acid catalysed degradation at 20°C (*Figure 1*) and those found for sulphuric acid concentrations 4.00×10^{-2} and 6.00×10^{-2} mol dm^{-3} at the same temperature (not shown) are in agreement with the proposed first-order rate equation (*equation 1*). Curvature of the kinetic plots, more noticeable in the case of sulphuric acid, can be ascribed to a secondary side-reaction between catalyst and acetic anhydride. This reaction, resulting in a gradual fall in effective catalyst concentration with time, is believed to be characteristic of all chloroalkane–acetic anhydride media and has been discussed earlier[1,2]. The use of initial rate constants ($t = 0$) in such cases is justified by the monotonic dependence of rate constant on catalyst concentration and the satisfactory Arrhenius plots observed here in tetrachloroethane and other solvents[1,2]. Increased curvature of the kinetic plots at higher temperatures, particularly in the case of sulphuric acid (*Figure 2*) may be accounted for by the temperature dependence of the side-reaction.

Perchloric acid is a much stronger catalyst than sulphuric acid, rates of degradation only becoming comparable when pechloric acid concentrations are a tenth of those for sulphuric acid (*Table 1*). This tenfold difference in catalytic ability for these two acids was also found in chloroform[1] and dichloromethane[2] solvents.

With reference to *Table 2*, the energies of activation for both acid catalysts are apparently independent of catalyst concentration, as expected. Average values for E_a in the case of perchloric and sulphuric acid are 87.7 and 91.4 kJ mol^{-1}, respectively, which are rather higher than those in chloroform[1] (74.1 and 55.6) or dichloromethane[2] (77.5 and 60.9) for the same acetic anhydride concentration of 2.12 mol dm^{-3}. These activation energies are comparable with those reported for fast bond scission in the heterogeneous degradation of cellulose with aqueous $KHSO_4$ solution[5].

Reaction mechanism

Chain scission of CTA under anhydrous conditions in the presence of acetic anhydride is believed to occur by means of an acetolysis mechanism[2] with the relevant equilibria being set up as follows:

$$HClO_4 \rightleftharpoons H^+ + ClO_4^- \qquad (2)$$

$$HClO_4 + Ac_2O \rightleftharpoons Ac^+ + ClO_4^- + AcOH \qquad (3)$$

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \qquad (4)$$

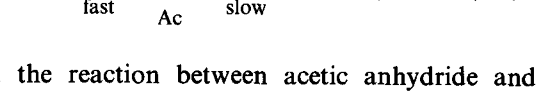
$$H_2SO_4 + Ac_2O \rightleftharpoons Ac^+ + HSO_4^- + AcOH \qquad (5)$$

The observed degradation rate constant (k) can then be expressed in terms of the concentrations of the catalytic species H^+ and Ac^+ (acetylium ion CH_3CO^+) with their respective catalytic coefficients k_{H^+} and k_{Ac^+} as shown by:

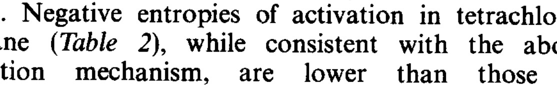
$$k = k_{H^+}[H^+] + k_{Ac^+}[Ac^+] \qquad (6)$$

Equilibria (2)–(5) are assumed to be rapidly established, with the concentrations $[H^+]$ and $[Ac^+]$ being determined by the relevant equilibrium constants. These equilibria thus account for the observed difference in rate constants and overall catalytic coefficients for the two acids. The much higher catalytic coefficients for $HClO_4$ at 20 and 25°C reported above can be ascribed to much greater values of the equilibrium constants for reactions (2) and (3) compared with reactions (4) and (5) for H_2SO_4. Direct evaluation of the degradation rate constant from total catalyst concentration, in a given chloroalkane solvent, clearly awaits a knowledge of the above equilibrium constants, their temperature coefficients, and the catalytic coefficients k_{H^+} and k_{Ac^+}. These factors appear to be influenced by acetic anhydride concentration since the latter has a marked effect on the rate constant in chloroform[1]. A reasonable assumption is that $k_{H^+} > k_{Ac^+}$, which would be a contributing factor to the increasing dependence of rate constant on catalyst concentration as the catalyst concentration increases (*Table 1*).

Chain scission for cellulose triacetate is believed to take place via two possible reaction sequences:



$$-O- \xrightarrow[\text{fast}]{H^+} -\underset{H}{\overset{+}{O}}- \xrightarrow[\text{slow}]{Ac_2O} -OAc + AcO^- + H^+ \qquad (7)$$



$$-O- \xrightarrow[\text{fast}]{Ac^+} -\underset{Ac}{\overset{+}{O}}- \xrightarrow[\text{slow}]{Ac_2O} -OAc + AcO^- + Ac^+ \qquad (8)$$

with the reaction between acetic anhydride and the charged intermediate complex being the rate determining step. Negative entropies of activation in tetrachloroethane (*Table 2*), while consistent with the above reaction mechanism, are lower than those in dichloromethane, which may reflect differences in extent of chloroalkane solvation of CTA and acetic anhydride. In the above reactions H^+ is written instead of the solvated form $AcOH_2^+$ since the former is believed to be the effective catalytic species.

Influence of solvent on degradation rate

The role of solvent is clearly a complex one, since the way in which it affects the equilibria (2)–(5) depends partly on its solvation ability for both acetic anhydride and the catalytic species. Differences in degree of solvation of CTA by chloroalkane solvents, while affecting the entropy of activation, may also modify the accessibility of oxygen linkages to acetic anhydride attack (equations 7 and 8). This may arise from steric hindrance by attached solvent molecules as well as changes in the CTA molecular chain configuration in different chloroalkane–acetic anhydride mixtures.

At present it is only possible to compare rates of degradation in three chloroalkane solvents using experimental rate constants and those calculated from reported Arrhenius parameters[1,2] for the temperature range 15–45°C. Solvents are compared with the same acetic anhydride concentration ($2.12\,\mathrm{mol\,dm^{-3}}$) and CTA concentration ($0.800\,\mathrm{g\,dl^{-1}}$) for both acid catalysts.

For perchloric acid catalyst the rates of degradation are in the solvent order chloroform > dichloromethane > tetrachloroethane for all catalyst concentrations up to $7.20\times10^{-3}\,\mathrm{mol\,dm^{-3}}$ and temperatures not exceeding 25°C. Above 25°C and for catalyst concentrations greater than $5.40\times10^{-3}\,\mathrm{mol\,dm^{-3}}$ the rates are in the order $CHCl_3 > CH_2Cl_2 \simeq C_2H_2Cl_4$ at 30°C and becoming $CHCl_3 > C_2H_2Cl_4 > CH_2Cl_2$ at higher temperatures.

In the case of sulphuric acid catalyst rates of degradation follow the solvent order $CHCl_3 > CH_2Cl_2 > C_2H_2Cl_4$ for the lowest catalyst concentration ($2.00\times10^{-2}\,\mathrm{mol\,dm^{-3}}$) up to 25°C, above which the order becomes $CHCl_3 > C_2H_2Cl_4 > CH_2Cl_2$. This change in solvent order occurs at lower temperatures as the catalyst concentration increases: thus for catalyst concentrations 3.00×10^{-2} and $4.00\times10^{-2}\,\mathrm{mol\,dm^{-3}}$ the solvent order is $CHCl_3 > CH_2Cl_2 > C_2H_2Cl_4$ up to 20°C, becoming $CHCl_3 > C_2H_2Cl_4 > CH_2Cl_2$ at higher temperatures. For the highest sulphuric acid concentration studied ($6.00\times10^{-2}\,\mathrm{mol\,dm^{-3}}$) the solvent order is $CHCl_3 > CH_2Cl_2 \simeq C_2H_2Cl_4$ at 15°C, which changes to $CHCl_3 > C_2H_2Cl_4 > CH_2Cl_2$ at all temperatures between 18 and 45°C.

If, as suggested in the introduction, the same catalytic mechanism applies to the acetylation of cellulose we might expect the above solvent orders to be also found for the rates of cellulose acetylation. To the authors' knowledge no such comparative acetylation studies have so far been reported in the literature.

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