

THE KINETICS OF THE OXIDATIVE DEGRADATION OF CELLULOSE AND CELLULOSE DOPED WITH CHLORIDES *

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ABSTRACT

The kinetic parameters of the thermal decomposition in air of pure α -cellulose and the same cellulose impregnated with calcium chloride, potassium chloride, sodium chloride and zinc chloride have been obtained using an isothermal mass loss method. The results from these experiments can be shown to agree closely with kinetic parameters obtained by other workers using a variety of techniques for the pyrolytic degradation of cellulose. It can be shown that the introduction of each chloride produces a different kinetic behavior as identified by the form of the mass loss curves corresponding to the various theoretical kinetic models. A compensation plot is observed relating the logarithm of the pre-exponential term with the activation energy. It is thought that the activation energies reported here may be associated predominantly with the formation of carbon monoxide and carbon dioxide.

INTRODUCTION

In this study the oxidative thermal degradation of cellulose is reported on the basis of isothermal mass loss experiments. Similar analyses based on the use of other techniques have been reported. Kinetic parameters for cellulose decomposition have been obtained not only from isothermal mass loss data [1–13] but also from rising temperature thermal analysis data [14–21], evolved gas detection results [22–25], density change measurements [26], determination of the degree of polymerization [27,28] and chemical analysis

* Our wishes for a Happy Birthday for Professor Wendlandt. May he continue in his scientific activities. Also in grateful recognition of a sincere and very likeable colleague.

[29,30]. The isothermal mass loss results under review were obtained in atmospheres of helium [8], nitrogen [2,4,6,7,9], static air [1,11] or under vacuum [1]. The experiments reported by Ross and co-workers [12,13] employed conditions similar to ours, i.e. isothermal experiments performed with samples in a flowing air atmosphere. The techniques employed to measure the isothermal mass loss of cellulose vary considerably, and the nature of the cellulose samples investigated also varied.

The literature values for the activation energy of the vacuum pyrolysis of cellulose vary between 192 kJ mol^{-1} reported by Holpern and Patai [5] and 208 kJ mol^{-1} reported by Madorsky et al. [10]. The activation energy values for the decomposition in nitrogen appear somewhat lower at $142\text{--}144 \text{ kJ mol}^{-1}$ [2,6,9]. For the decomposition of cellulose in air, Shivadev and Emmons [1] reported an activation energy of 226 kJ mol^{-1} . Typical values obtained by Ross and co-workers [12,13] for the decomposition in air are 163 and 181 kJ mol^{-1} . The choice of the kinetic equation to describe the behavior can also be the cause of some divergence of the activation energy values. Values proposed for the order of the isothermal cellulose decomposition are zero [6], first order [8] and then a combination of zero and then first [9], or half and then first [4]. Dollimore and Holt [2] found the Avrami–Erofeev equation gave the best fit to their experimental data for degree of decomposition up to 0.6. Ross and co-workers also found that an interpretation was possible in terms of the above equation or similar equations. It should also be stated that the highest reported activation energy for the degradation process obtained by a rising temperature technique is 250 kJ mol^{-1} , while the lowest recorded value is 73 kJ mol^{-1} , both results having been obtained from experiments under vacuum. Murphy [25] used a McLeod gauge to measure the pressure of gas evolved from the pyrolysis of cellulose at temperatures as low as 140°C and calculated the activation energy to be 142 kJ mol^{-1} . From the rates of formation of carbon dioxide and carbon monoxide, Baker [22] calculated activation energies between 30 and 75 kJ mol^{-1} . McCarter [23] also used an evolved gas technique but found activation energies which were higher.

In the present studies the cellulose was also impregnated with the chlorides of calcium, potassium, sodium and zinc. The choice of these materials was governed by the fact that they had been used in other studies [31–34].

Differential thermal analysis (DTA) and thermogravimetric (TG) studies on cellulose degradation in an oxidizing atmosphere have been carried out by the present authors [35]. These indicate an initial process in air similar to the endothermic decomposition process in nitrogen [2] except that an exothermic character is imparted to the reaction by the combustion of the volatile gas products. This had a bearing on the temperature range over which reliable isothermal kinetic data could be obtained.

EXPERIMENTAL

Cellulose

The cellulose used was an α -cellulose powder described as Whatman CC31 and used by the present authors in previous studies [2,35]. It has a rod-like form and contains the following levels of impurity: ash, max., 0.01%; iron, 5 p.p.m.; copper, 2 p.p.m.).

Impregnated samples

Impregnated samples of cellulose were prepared using calcium, potassium, sodium and zinc chlorides (of AnalaR quality). An impregnation level of 2–3% (w/w) was chosen for each of the salts as this appeared typical of the other published reports. The impregnation levels found by chemical analysis are as follows: calcium chloride impregnated sample (impregnation level expressed as %Cl, w/w), 2.96%; potassium chloride, 2.54%; sodium chloride sample, 2.67%; zinc chloride sample, 2.67%. The treated cellulose was dried for 1 day at 110 °C and then stored in a desiccator over silica gel.

Modified microbalance used to follow kinetics

A modified CI Mk.2 microforce balance was used for the isothermal loss experiments. A platinum stirrup and crucible were used. There were no detectable buoyancy effects in studies reported in this work. The thermocouples were of chromel–alumel and a cold junction at 0 °C was included in the circuitry. The sample thermocouple was placed just below the crucible and separated from it in use by a distance of 1 mm. A supply of dry air was used at a flow rate of 12 ml min⁻¹. The air flowed into the balance case, down the hangdown tube to be discharged just below the sample, thus preventing tars evolved from the cellulose from condensing on the balance mechanism.

RESULTS AND DISCUSSION

Figure 1 shows the plot of percentage mass loss against time for the pure cellulose heated in air at a series of temperatures (208, 216, 224, 232 and 240 °C). Runs at these temperatures were repeated on all the other impregnated samples. The final mass loss was approached asymptotically. To assess the final mass loss, a plot was made in all cases of the percentage mass loss against reciprocal time and an estimate obtained by extrapolating the line to zero reciprocal time (see Fig. 2). Once the final mass loss had been established, then the data could be transposed into plots of the degree of decomposition (α) against time (t) and the time for 50% reaction ($t_{0.5}$) could

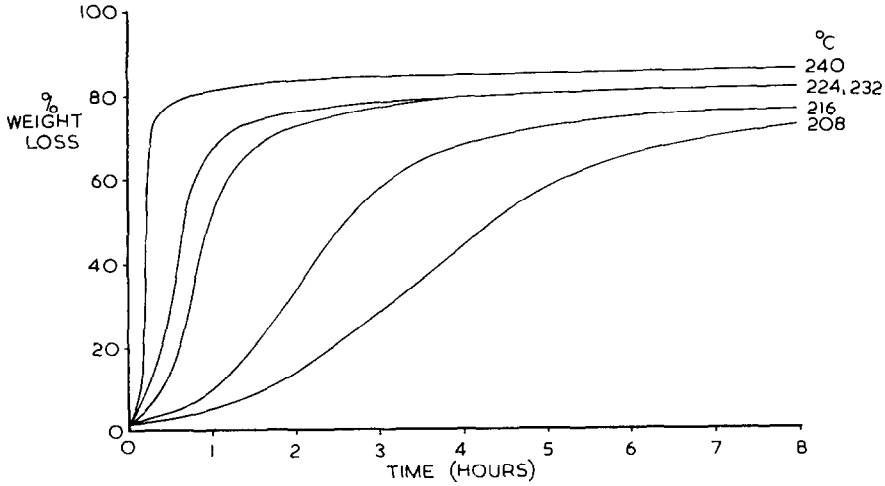


Fig. 1. Isothermal mass loss data in air for pure cellulose.

be determined. A reduced time plot of α against $t/t_{0.5}$ could be constructed and used to test the isokinetic nature of the process at different temperatures and the probable kinetic equation ascertained [36] (Fig 3). The data were only collected in temperature ranges where the reaction could be controlled and was not self-propagating. This procedure enabled the kinetic law to be identified for each of the impregnated celluloses and the specific reaction

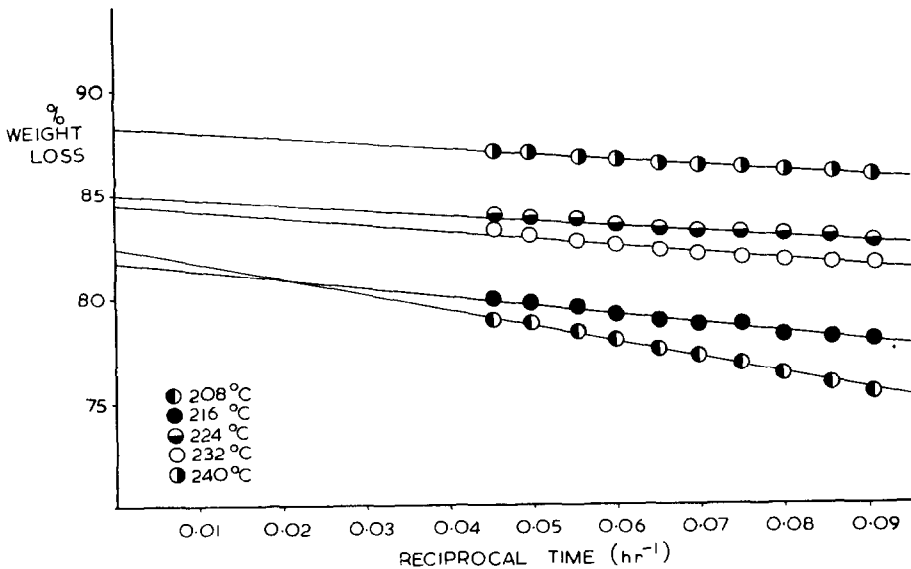


Fig. 2. Typical plot of reciprocal time versus percentage mass loss for pure cellulose.

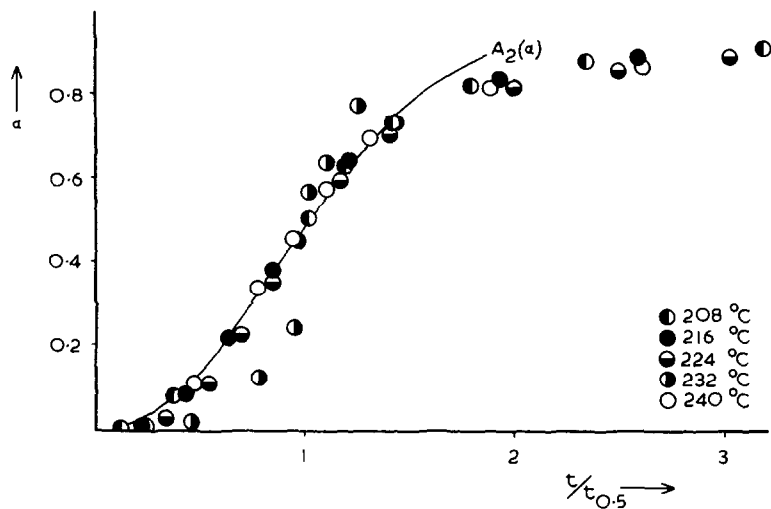


Fig. 3. Typical reduced time plot for pure cellulose.

rate to be calculated at each temperature thus facilitating the calculation of the Arrhenius parameters by plotting $\ln k$ against reciprocal temperature (K) (see Fig. 4). The data shown in this report to illustrate the method are for pure cellulose. The runs at 208, 216, 224 and 232°C were all isokinetic but the experiment at 240°C was not. It was found that under the conditions of the experiment the ignition temperature appeared to be between 232 and 240°C (the heat generated at 240°C by ignition of the cellulose was

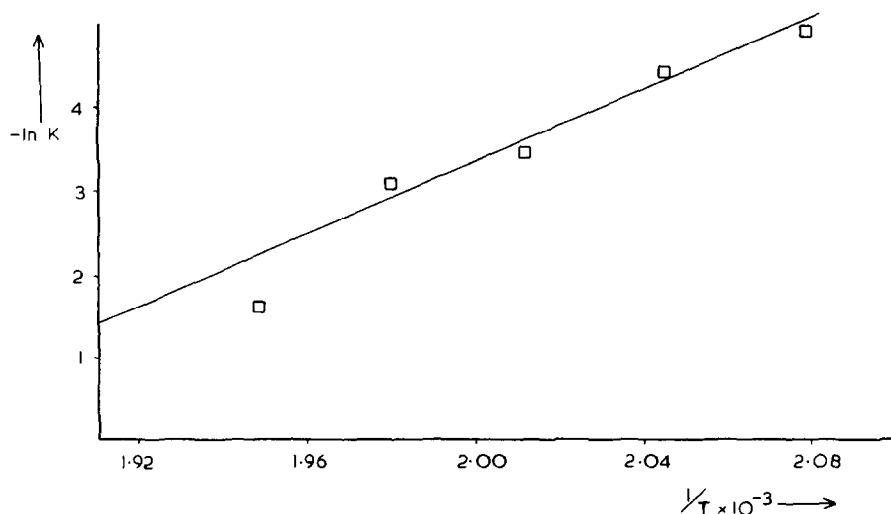


Fig. 4. Arrhenius plot of isothermal decomposition of pure cellulose in air.

sufficient to increase its temperature by 12°C). The 240°C experiment on cellulose was not used to calculate the Arrhenius parameters. It is seen that the analysis suggests that the Avrami–Erofeev equation (with $n = 2$) is obeyed for the thermal decomposition of pure cellulose in air. This takes the form

$$1 - \alpha = e^{-kt^n}$$

written in the reduced time form as

$$\begin{aligned} A_2(\alpha) &= [-\ln(1 - \alpha)]^{1/n} \\ &= Kt = 0.8326(t/t_{0.5}) \end{aligned}$$

where $n = 2$, α is the fractional decomposition at time t , $t_{0.5}$ is the time for α to reach 0.5 and k is a constant at the temperature of the run. An investigation of the thermal decomposition of pure cellulose in nitrogen [2] has already shown similar obedience to the Avrami–Erofeev equation. This expression with $n = 2$ is said to describe reactions occurring by random nucleation and nucleus growth in cylindrical particles.

The isothermal mass loss data for calcium chloride-impregnated cellulose were analyzed in a similar way and showed that the most relevant kinetic process is that for a two-dimensional diffusion-controlled reaction in a cylinder. This takes the form

$$(1 - \alpha) \ln(1 - \alpha) + \alpha = \frac{Kt}{r^2}$$

or

$$\begin{aligned} D_2(\alpha) &= (K/r^2)t \\ &= Kt = 0.1534(t/t_{0.5}) \end{aligned}$$

where r is the radius of the cylindrical particle.

The potassium chloride-impregnated sample showed kinetic data with a constant reaction rate (i.e. a zero-order reaction) up to $\alpha = 0.6$. An adequate fit could also be obtained using a kinetic expression for two-dimensional growth. This is of the form

$$\begin{aligned} 1 - (1 - \alpha)^{1/2} &= Kt \\ R_2(\alpha) &= [1 - (1 - \alpha)^{1/2}] \\ &= \frac{V}{r}t = 0.2929t/t_{0.5} \end{aligned}$$

where V is the velocity of movement of the interface. Both the zero-order equation and the $R_2(\alpha)$ equation were used in calculating the Arrhenius parameters. In this series of experiments the runs at 240°C were discounted because of self-ignition. The sodium chloride samples behaved similarly to the potassium chloride samples. The sample decomposing in air at 240°C, however, did not self-ignite and so was included in the calculation of the

TABLE 1

Summary of kinetic results (data in parentheses are those used for Fig. 5 and are based on a first-order law)

Sample	Activation energy (kJ mol ⁻¹)	Pre-exponential factor (s ⁻¹)	Kinetic law	Range
Pure cellulose	163 (150)	3.59×10^{15} (1.26×10^{14})	A ₂ (α)	0.2–0.8
CaCl ₂ -impregnated cellulose	142 (149)	2.40×10^{12} (4.9×10^{13})	D ₂ (α)	0.25–0.75
KCl-impregnated cellulose	136	1.58×10^{12}	R ₂ (α)	0–0.6
	138 (105)	2.46×10^{12} (9.20×10^8)	Zero order	0–0.6
NaCl-impregnated cellulose	146 (109)	1.48×10^{13} (2.64×10^9)	Zero order	0–0.55
ZnCl ₂ -impregnated cellulose	181 (188)	4.07×10^{17} (4.54×10^{18})	D ₂ (α)	0–0.5

Arrhenius parameters. The data fitted a zero-order mechanism up to $\alpha = 0.55$.

The zinc chloride-impregnated cellulose gave data on heat treatment runs in air which were isokinetic at temperatures up to and including the run at 240°C and analyzed best by the D₂(α) equation. Table 1 summarizes the calculated Arrhenius parameters for all the samples investigated. It can be shown that a compensation effect operates. To check this, the kinetic laws were all recalculated on the same basis of a first-order decay equation to give the compensation plot shown in Fig. 5.

It is reasonable to question some of the basic assumptions made in the calculation of kinetic data. A direct link between the continuous record of the total mass of a decomposing material and the rate-determining step of the decomposition process is difficult to prove. Consequently the activation energy obtained using this technique may be more a function of the particular experiment and experimental conditions than some fundamental parameter of the degradation. Similarly it would be unwise to claim (without additional evidence) that since an experimental decomposition curve approximately fits a particular equation, the decomposition geometry corresponding to the equation also applies to the experimental system. The experiments on cellulose impregnated with potassium chloride have indicated that any mathematical expression which approximately describes a decomposition can be used to provide a close estimate of the activation energy.

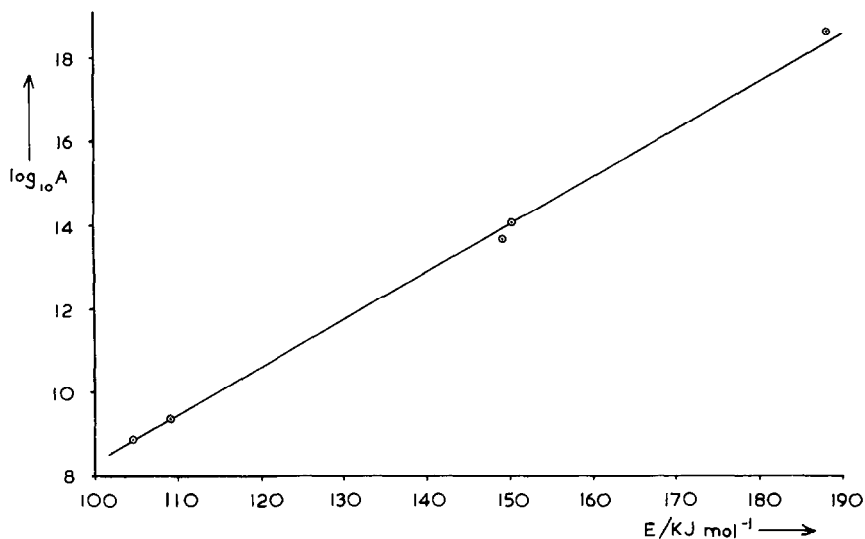


Fig. 5. Compensation plot ($\log A$ vs. E) for pure and treated cellulose.

It has been shown that the Avrami–Erofeev ($n = 2$) equation holds equally well in air (at sub-ignition temperatures) for the thermal degradation of pure cellulose as in nitrogen [2]. It has also been demonstrated that the addition to cellulose of less than 3% of each of the four chlorides investigated produces radical changes in the kinetics of its decomposition. Furthermore, each chloride affects the decomposition in a different way, although the effects of the sodium and potassium salts are similar. The decomposition of cellulose impregnated with sodium and potassium chloride has been shown to follow, approximately, both zero-order kinetics and the expression for two-dimensional growth while for cellulose treated with calcium and zinc chloride the best fit has been obtained by the equation for a two-dimensional diffusion-controlled reaction. If it were shown that two-dimensional growth or diffusion actually control these decompositions, and that random nucleation and nucleus growth in cylinders occur in the decomposition of pure cellulose, then it could be postulated that these salts act as flame retardants by means of physical effects on the geometries of the decomposing systems. Different authors have proposed several values for the order of the reaction as a consequence of their particular experimental results. If some of these experiments had been performed on impure cellulose, then the contaminant may have changed the decomposition kinetics, thus affecting the order of the reaction, similar to the effects of the chlorides reported here.

The conclusion sometimes inferred from the observation that a compensation plot is operative is that there are several types of reaction sites, each identified by characteristic Arrhenius parameters (i.e. pre-exponential term A and activation energy E) and that these different types of sites are all

involved simultaneously in any one kinetic experiment [37,38]. The term that alters is the number of each type of site involved on progression from one experiment to another. The alternative view is that the compensation plot is simply some function of the experimental procedure and the use of the Arrhenius equation. The first theory has been shown to result in a linear relationship between $\log A$ and the E but the second hypothesis has not been shown to require such a linear relationship. It has been shown from the experimental results reported here that a compensation plot can be obtained from the kinetic parameters of the thermal decomposition of pure and treated cellulose, including those parameters obtained from experiments where ignition occurred. These results cannot be said to give additional support to either of the two viewpoints.

From the isothermal weight loss experiments, it appears that the relative merits of the individual chlorides with respect to the ignition temperature are

pure, $\text{KCl} < \text{CaCl}_2, \text{ZnCl}_2$

If the values of the activation energy are compared to each other then

pure $> \text{ZnCl}_2 > \text{CaCl}_2 > \text{KCl}$

Levoglucosan yields from the thermolysis of pure and treated cellulose have been obtained by Golova and Krylova [30,32] and by Tsuchiya and Sumi [33]. The relative performance of each of the impregnated samples from their results are: levoglucosan yield

pure $> \text{ZnCl}_2 > \text{CaCl}_2 > \text{KCl}$

Tsuchiya and Sumi's results also give: CO yield

pure $< \text{ZnCl}_2 < \text{CaCl}_2 < \text{KCl}$

CO_2 yield

pure $< \text{ZnCl}_2 < \text{CaCl}_2 < \text{KCl}$

The sequence for the activation energy is in the same order as the yields of levoglucosan and in reverse order to the yields of carbon monoxide and carbon dioxide. Therefore, it may be suggested very tentatively that the activation energies calculated by the isothermal mass loss method are parameters associated predominantly with the formation of carbon dioxide and carbon monoxide.

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