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IS THE BROIDO - SHAFIZADEH MODEL FOR CELLULOSE PYROLYSIS TRUE?[†]

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[†]This paper is dedicated to Dr. Abraham Broido in recognition of his many contributions to the fields of cellulose pyrolysis and combustion.

ABSTRACT

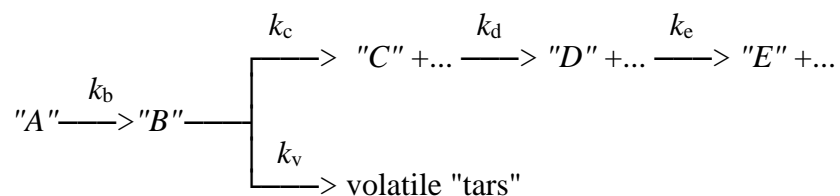
The widely accepted Broido-Shafizadeh model describes cellulose pyrolysis kinetics in terms of two parallel (competing) reactions preceded by an initiation step. In spite of the fact that many recent experimental results seem to contradict the predictions of the model, its validity has not been seriously questioned. In this paper we report thermogravimetric analyses of Avicel cellulose involving prolonged thermal pretreatments of small samples (0.5 to 3 mg). The weight loss curves were simulated by modern numerical techniques using the Broido-Shafizadeh and other related models. Results were not consistent with the presence of an initiation reaction, but they did strongly confirm the role of parallel reactions in the decomposition chemistry. A subsequent, high temperature (370 °C), pyrolytic degradation of solid intermediates formed below 300 °C was also detected. In the absence of a prolonged thermal

pretreatment, only one of the two parallel reactions can be observed. This reaction is first order, irreversible, and manifests a high activation energy (238 kJ/mol). The kinetic parameters of this reaction are not influenced by the large quantity of solid intermediates formed during prolonged, low-temperature thermal pretreatments, indicating that chemical processes are much more significant than the physical structure of the sample during pyrolysis.

INTRODUCTION

Lignocellulosic biomass materials are an important part of the energy resource pool that mankind draws upon; consequently the thermal behavior of their constituents commands considerable interest. Cellulose composes up to 50% of these materials and its thermal decomposition is strongly influenced by experimental conditions. Depending upon the purity and size of the sample, cellulose pyrolysis can result in the formation of either the monomeric anhydrosugar levoglucosan and related species¹, or char² and light volatile fragmentation products such as glycolaldehyde³⁻⁶. In this paper we deal only with the pyrolysis kinetics of pure, ash-free cellulose under conditions where secondary reactions and transport processes do not obfuscate the primary solid-phase decomposition reactions.

The first kinetic model with predictive capabilities that captured some of the complexity of cellulose pyrolysis was developed in a series of seminal papers by Broido and his coworkers⁷⁻⁹. We summarize this model in scheme 1 below:



Reaction Scheme 1

In scheme 1 "A" denotes the cellulose substrate, which reacts at elevated temperatures to form a so called "active cellulose", "B", with rate constant k_b . The active cellulose decomposes further by two competitive mechanisms, producing either volatiles (without char), or solid intermediates "C", "D" and "E" via a sequence of consecutive reactions. The ellipses with the plus sign, "+ ...", indicate accompanying volatile formation. The temperature dependence of each of the rate constants is approximated by the Arrhenius equation:

$$k_i = A_i \exp (E_i / RT) \quad i = b, c, d, e, v \quad (1)$$

Later Bradbury, Sakai and Shafizadeh¹⁰ simplified Broido's reaction network by omitting the reactions leading to "D" and "E" in the upper branch. This simplified reaction scheme, called the "*Broido-Shafizadeh model*", is generally accepted today and the kinetic parameters presented by Bradbury et al.¹⁰

are frequently quoted and used in simulations^{4,6,11-13}. Nevertheless, scheme 1 can be criticized as an oversimplification of extremely complex chemical and physical phenomena. One rationale for the modeling of complicated organic reactions by simplified reaction schemes is that a partial reaction in the scheme may correspond in reality to a group of reactions. For example, a partial reaction may be the average of several parallel reactions or the slowest step in a sequence of consecutive reactions.

Experimental studies of the influence of prolonged thermal pretreatments on char yields from pure cellulose were the foundation of Broido's modeling efforts. In spite of their importance, Broido's experimental findings have not been reproduced or confirmed by any subsequent researchers. Mok and Antal¹⁴ (1983), Zaror and Pyle¹⁵ (1986), Várhegyi et al.¹⁶ (1988a), Piskorz et al.¹⁷ (1989) and Antal et al.¹⁸ (1990) all reported that less prolonged thermal pretreatments exert only a small or even negligible influence on char yields. Moreover several recent workers¹⁹⁻²³ have been able to precisely mimic high quality cellulose weight loss curves using only a single step, irreversible, first order rate law. Possible explanations for these disagreements include:

(i) Broido et al.⁷⁻⁹ employed comparatively large (90 mg) samples of Whatman #541 filter paper. Similarly, Bradbury et al.¹⁰ worked with 250 mg samples of Whatman CF 11 filter paper. It is not possible to exclude *a priori* the possibility that diffusion of the pyrolytic vapors through these relatively large samples led to secondary reactions which could obscure the underlying decomposition chemistry. In addition, as emphasized by Bradbury et al.¹⁰, heat transfer problems were evident in their highest temperature (335°C) isothermal experiment, where the sample mass decreased from 90 to 35 % within a time of ca. 2 minutes.

(ii) Modern computer hardware and software permit better data acquisition and much more powerful numerical simulations than in the seventies. At that time it was not possible to examine numerically the necessity for a given reaction step in a complex reaction network. We now know that in some cases the loss of a postulated reaction from a model can be compensated by proper adjustment of the remaining kinetic parameters. Broido and Weinstein⁷ used an analog computer in their modeling work. The best fitting solution was selected following a visual comparison of the simulated and experimental curves displayed on an oscilloscope. A digital computer was used only to reveal fine details that were not visible on the oscilloscope. Bradbury et al.¹⁰ started with an analytical solution to an isothermal model which contained only reactions *c* and *v*. Their evaluation employed a visual fitting of straight lines to experimental data on semi-logarithmic graph paper. Similarly, the activation energy of reaction *b* was determined by use of an Arrhenius-plot of the positions of the maxima of the first derivative of the weight loss curves. Only the pre-exponential factor of reaction *b* was determined by numerical integration of the governing ordinary differential equations (ODE's) and curve fitting. The integration of a system of ODE's over a non-isothermal temperature-time history was out of question in these studies; consequently events

which occurred during the initial heat-up or while heating from one isothermal temperature to another could not be taken into account at that time.

(iii) Expanding on ii) above, the work of Bradbury et al.¹⁰ was based on only four isothermal weight loss curves, and each of the curves was defined by only 5 - 7 experimental measurements. The first 50 % of the mass loss was represented by only 3 or 4 points on each curve. Consequently, the selection of the highest slope points required for their method of evaluation was dubious at best.

In light of the above, we undertook this study with the goal of determining what aspects of the earlier work remain valid, and what changes may be necessitated to enable the Broido-Shafizadeh model to explain the results of recent workers. We wish to emphasize that the work of Broido and Weinstein⁷, Broido⁹ and Bradbury et al.¹⁰ was unquestionably outstanding, especially considering the fact that most researchers in the field of thermal analysis at that time only attempted evaluations which involved a *single* Arrhenius equation using calculators or semi-logarithmic paper.

EXPERIMENTAL

Apparatus and materials. As in our earlier work^{16,21} pure microcrystalline cellulose, Avicel PH – 105, obtained from the FMC Corporation was used as a substrate. This material is easily acquired and serves as a standard substrate for the field. Its average particle size, degree of polymerization, crystallinity, and ash content were specified to be 30 μ m, 240 units, 92%, and 40 ppm. A Perkin Elmer TGS–2 thermobalance equipped with a 12 bit A/D converter and a computer was used to measure weight loss and the temperature-time history of the sample. To avoid heat and mass transfer problems, low sample masses (2 - 3 mg) and low heating rates (10 °C/min) were usually employed. Since the highest reaction rate in a given TG curve, $(-dm/dt)_{\text{peak}}$, is roughly proportional to the heating rate during linear $T(t)$ experiments, the sample mass was reduced to 0.5 - 0.6 mg when higher heating rates (50 - 80°C/min) were used. The grains of the sample were evenly distributed over an open, 6 mm diameter, platinum sample pan. High purity argon with a flow rate of 140 mL/min was employed as the purge gas. A few test experiments were conducted using a purge of high purity helium. The oxygen content of the argon and helium was ca. 10 and 1 ppm, respectively. The samples were dried inside the thermobalance before the start of the experiment.

Linear heating program experiments. Five experiments were carried out in argon with a heating rate of 10°C/min to determine the reproducibility of the kinetic parameters. An additional measurement with an initial sample mass of 0.5 mg was executed to discern the effects of heat and mass transfer

intrusions. Three linear $T(t)$ experiments were executed in flowing helium with heating rates of 2, 10 and $50^{\circ}\text{C}/\text{min}$. The results of 11 earlier, linear $T(t)$ experiments, measured over an 8 year period, were also used to determine the mean values and standard deviations of the kinetic parameters. Heating rates of 5, 10, 20 and $80^{\circ}\text{C}/\text{min}$ were employed in this group. Four of these experiments were described in earlier publications^{16,21}

Heating programs containing isothermal sections. To investigate the pyrolytic events which occur at lower temperatures, 8 experiments were conducted. Isothermal sections of 999, 60 and 30 minutes were connected by temperature ramps of $40^{\circ}\text{C}/\text{min}$ (see Table 1.). The isothermal section at 370°C was selected to mimic the work of Broido and Nelson⁸. The last 30 min section at 500°C was included to determine the final char yield. Although Broido and Nelson defined "char" to be the solid residue obtained at 370°C , the term "char" as it is used today more often refers to a residue obtained at a higher temperature. Experiments 1 - 5 were used in the simultaneous curve fitting process described below. Experiments 6 and *H* were used to check the stability of the "char" at 370°C as well as the effect of using helium instead of argon as the purge gas.

Table 1: Temperature programs of the isothermal experiments^a

Experiment	ISOTHERMAL SECTIONS			SOLID RESIDUE ^b (%)		
	1	2	3	290°C	370°C	500°
1	-	120 min / 370°C	30 min / 500°C	99	53 → 4	4 → 3
2	120 min / 250°C	60 min / 370°C	30 min / 500°C	96	53 → 5	4 → 4
3	999 min / 250°C	60 min / 370°C	30 min / 500°C	74	33 → 9	8 → 7
4	999 min / 260°C	60 min / 370°C	30 min / 500°C	47	23 → 11	10 → 9
5	999 min / 275°C	60 min / 370°C	30 min / 500°C	18	17 → 12	11 → 9
6	999 min / 286°C	60 min / 370°C	30 min / 500°C	12	12 → 9	8 → 7
7	999 min / 275°C	999 min / 370°C	30 min / 500°C	17	17 → 10	9 → 9
H ^c	999 min / 260°C	60 min / 370°C	30 min / 500°C	35	19 → 11	10 → 9

^a A $40^{\circ}\text{C}/\text{min}$ linear heating program was intercepted by the isothermal sections indicated in the table.

^b Percent of the initial dry sample mass. The numbers before and after the arrows represent the amounts of solid residue at the beginning and at the end of the corresponding isothermal section.

^c Experiment H was conducted in flowing helium.

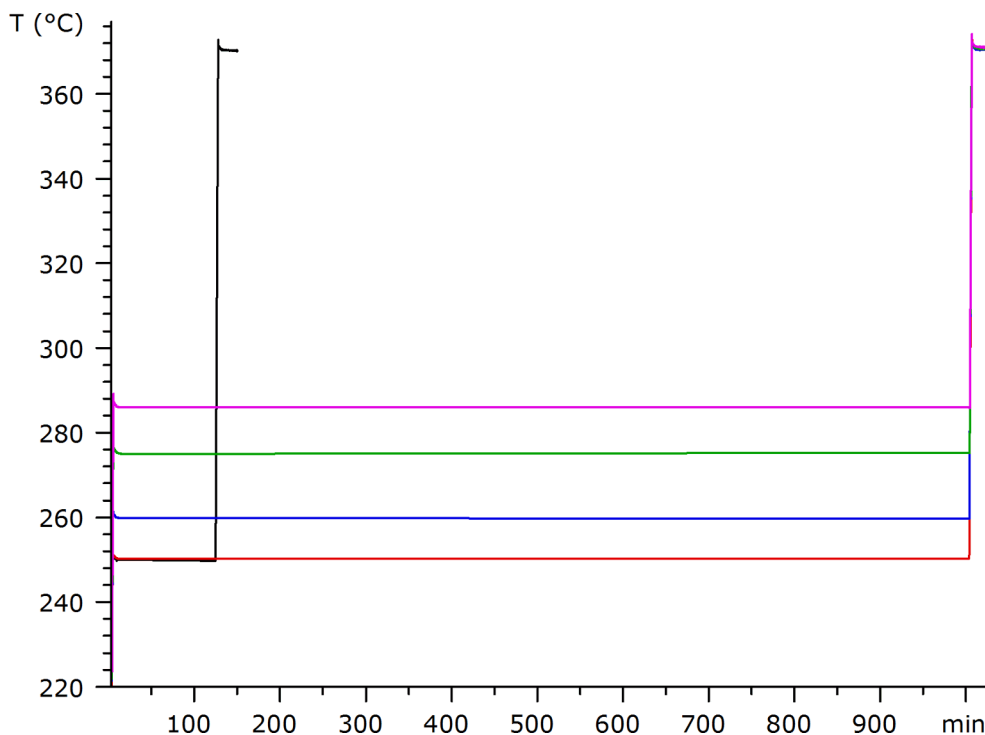


Figure S1. (Supplementary material to the published article.) The temperature programs of Experiments 2 – 6 are plotted here, as function of time, without their final heating section till 500°C. (See Table 1.) Color codes of the Experiments in this figure: 2, 3, 4, 5, 6.

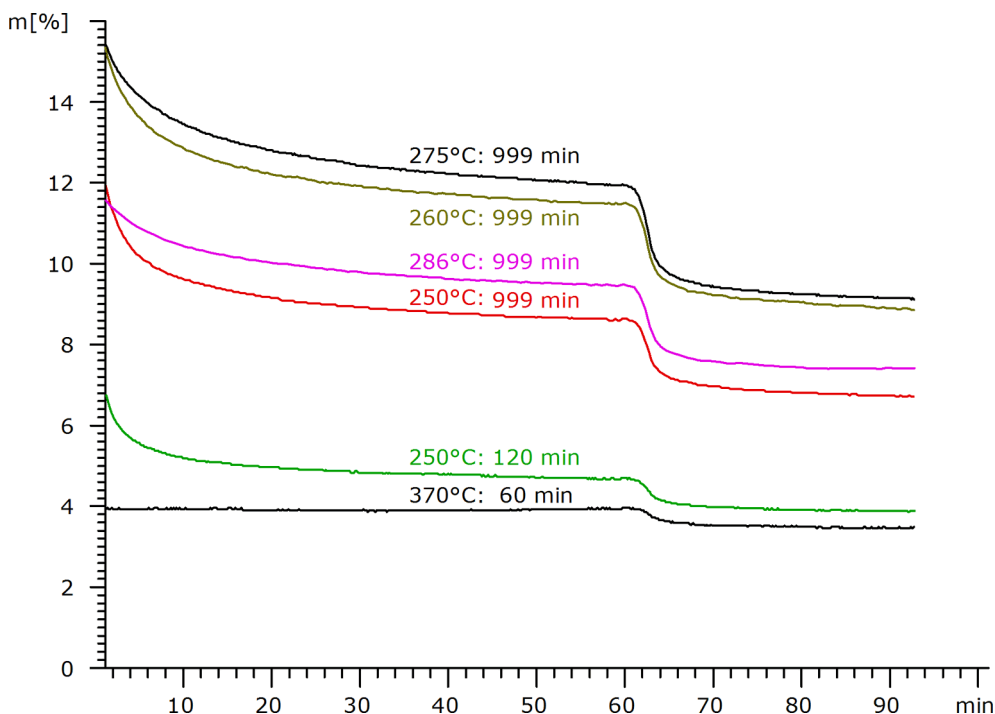


Figure S2. (Supplementary material to the published article.) The last 100 minutes of Experiments 1 – 6 (See Table 1.) The sample mass is shown as percent of the initial mass during a 1 hour isothermal section at 370°C followed by a half hour isothermal at 500°C. The characteristics of the earlier part of the T(t) function are written on the curves. Color codes of the Experiments in this figure: 1, 2, 3, 4, 5, 6.

MATHEMATICAL EQUATIONS

In Scheme 1 the yields of the solid intermediates will be denoted by y_c , y_d , and y_e , respectively. For example, the amount of solids "E" and vapors formed from a unit mass of intermediate "D" will be designated y_e and $1-y_e$, respectively. For the sake of generality, if we allow volatile formation during the first reaction, we should introduce the yield of solid intermediate "B", denoted by y_b , into the model.

The lower branch denotes a depolymerization-type volatilization with rate constant k_v . This reaction may also produce solids, e.g. by the secondary cracking of volatiles; hence we introduce an unknown parameter y_v into the model. Thus y_v denotes the yield of solid products associated with rate constant k_v . Broido and Weisntein^{7,9} assumed $y_v=0$.

Let m , S_b , S_c , S_d , and S_e denote the mass of the sample and the amounts of solid intermediates "B", "C", "D" and "E", respectively, as normalized by the initial sample mass. To retain a consistent notation, the normalized amounts of the unreacted cellulose and the char formed in the lower branch of scheme 1 will be denoted by S_a and S_v , respectively.

The following rate laws govern the appearance and disappearance of each component:

$$dS_a/dt = -k_b S_a \quad (2)$$

$$dS_b/dt = y_b k_b S_a - k_c S_b - k_v S_b \quad (3)$$

$$dS_c/dt = y_c k_c S_b - k_d S_c \quad (4)$$

$$dS_d/dt = y_d k_d S_c - k_e S_d \quad (5)$$

$$dS_e/dt = y_e k_e S_d \quad (6)$$

$$dS_v/dt = y_v k_v S_b \quad (7)$$

The mass loss of the sample is a sum of the mass losses of the partial reactions:

$$\begin{aligned} -dm/dt = & (1-y_b) k_b S_a + (1-y_c) k_c S_b + (1-y_d) k_d S_c + \\ & + (1-y_e) k_e S_d + (1-y_v) k_v S_b \end{aligned} \quad (8)$$

The initial conditions for equations (2) - (8) are

$$\begin{aligned} m(0)=1, \quad S_a(0)=1, \\ S_b(0) = S_c(0) = S_d(0) = S_e(0) = S_f(0) = S_v(0) = 0 \end{aligned} \quad (9)$$

From the definition of quantities y_i we have the following constraint:

$$0 \leq y_i \leq 1 \quad i = b, c, d, e, v \quad (10)$$

A major part of this paper deals with scheme 1 without the *cellulose* \longrightarrow *active cellulose* reaction. In this case equations (2), (3) and (8) are replaced by

$$dS_a/dt = -k_c S_a - k_v S_a \quad (11)$$

$$dS_c/dt = y_c k_c S_s - k_d S_c \quad (12)$$

$$\begin{aligned} -dm/dt = & (1-y_c) k_c S_a + (1-y_d) k_d S_c + \\ & + (1-y_e) k_e S_d + (1-y_v) k_v S_b \end{aligned} \quad (13)$$

NUMERICAL METHODS

Least squares curve fitting. Models for the weight loss data were evaluated by the method of the least squares. The fit of the model to the experimental data was defined as

$$fit (\%) = 100 (\sum \sum [m^{calc}(i,j) - m^{obs}(i,j)]^2 / N_j / M)^{0.5} \quad (14)$$

where M is the number of experiments used in the evaluation and N_j is the number of weight loss measurements obtained during the j th experiment.

In the linear $T(t)$ experiments the domain of evaluation included measurements taken before the reaction rate achieved a detectable level, and ended when the rate of mass loss, $-dm/dt$, decreased to 1 - 2 % of its peak value. In the non-linear $T(t)$ experiments the evaluation started around 220°C and ended at the conclusion of the 370°C isothermal section. A lower density of points was used to represent those sections where the reaction rate was extremely low. The calculations were carried out on an IBM compatible desktop computer under DOS. The programs were written in Fortran with double precision arithmetic and data storage.

Numerical solution of the ODE systems. Integration of the governing ODE's was initiated at a low temperature, 180°C, where all of the reaction rates were negligible. Linear interpolation was used to connect the $T(t_i)$ points. An adaptive step-size Runge Kutta method²⁴ proved to be an efficient integrator for the systems of equations appearing here. When the amount of a given species in the model decreased below a certain limit, e.g. 10^{-7} , and its parent, if any, was also consumed, the value of the corresponding variable was set exactly to zero. This blocked the corresponding reactions for the remainder of the integration. Without this strategem the ODE integrator would have been forced to select very small step sizes to cope with those rate constants which increased by factors of $10^3 - 10^4$ during the rise of temperature.

Minimization of the least squares sum. Since computer time is virtually free, a robust direct search method, the simplex method of Nelder and Mead was employed²⁴. The interdependence between parameters E and $\ln A$ was eliminated by the following parameter transformation:

$$Z_i = \ln A_i - E_i/RT_m \quad i = b, c, d, e, v \quad (15)$$

where each A_i was replaced by Z_i , and T_m is an arbitrarily chosen fixed temperature somewhere in the middle of the temperature interval. A typical run consisted of finding 12 - 14 unknown parameters by fitting simultaneously five 20-hour experimental curves, which required between 1 and 2 nights of computer time at a speed of 2×10^5 floating point operations per second.

RESULTS

Kinetics of the linear $T(t)$ experiments. Our experience shows that the upper branch of reaction scheme 1 can be detected only if the sample is thermally pretreated for a sufficiently long time below ca. 300°C. In other cases the lower branch dominates and the observed reaction rate can be well approximated by a single first order reaction. The dominance of the lower branch means that equations (3) - (10) are reduced to

$$dS_a/dt = -k_v S_a \quad (16)$$

$$-dm/dt = (1-y_v) k_v S_a \quad (17)$$

We evaluated the 21 linear $T(t)$ experiments assuming first order reaction kinetics in three different ways:

(i) Each experiment was analyzed separately from the others. The averages and standard deviations of the parameters and the deviation between the experimental data and the model data are shown in Table 2. The kinetic parameters evidenced a random scattering of ca. 5 %. The activation energy, $E_v = 238 \pm 10$ kJ/mol, is in good agreement with the value Broido⁹ reported for linear $T(t)$ thermogravimetric experiments (230 ± 8 kJ/mol).

(ii) During a second series of evaluations the activation energy was fixed at the average value obtained above: $E_v = 238$ kJ/mol. Table 2 shows that this constraint resulted in the same average value for the pre-exponential factors with a scattering of only 1.5 %. The corresponding fits, illustrated by Figure 1, were only slightly worse than in case (i).

(iii) As an alternate method, the 21 linear $T(t)$ experiments were evaluated simultaneously with identical A_v and E_v values. In this case ca. 10 times worse fit (4%) was obtained, the model curves were flatter than the experimental ones, and the kinetic parameters significantly differed from the results of

cases (i) and (ii). We found this method to be not suitable for the evaluation of the experiments and we did not include the corresponding parameters in Table 2. The failure of this approach to kinetic analysis of TG data is probably due to the fact that experimental errors associated with individual points of the curves are neither random nor independent.

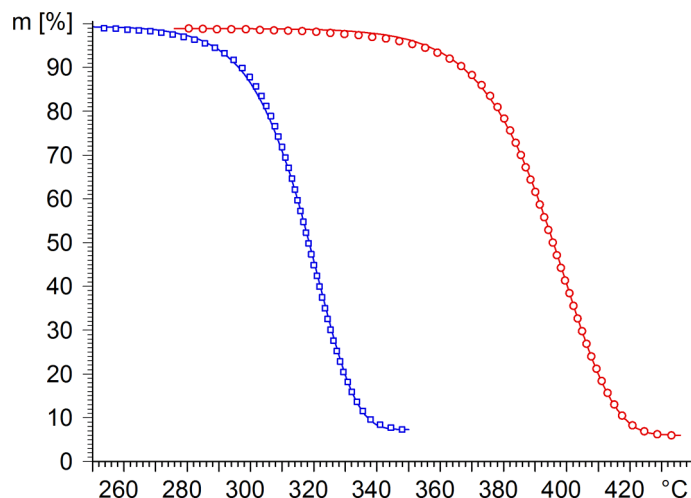


Figure 1. Kinetic evaluation of low and high heating rate, linear $T(t)$ experiments assuming a single step, first order kinetic model with $E_v = 238$ kJ/mol. Experimental conditions: 3 mg sample at $2^\circ\text{C}/\text{min}$ in flowing helium ($\square\square\square$); 0.5 mg sample at $80^\circ\text{C}/\text{min}$ in flowing argon ($\circ\circ\circ$). The solid curves represent the calculated curves.

Table 2: Evaluation of 21 linear $T(t)$ experiments and selected domains of 4 other experiments, by a single step kinetic model^a

Group of experiments	Constraint	Fit ^b %	E_v kJ/mol	$\log(A_v/s^{-1})$
21 linear $T(t)$ experiments	none	0.4 ± 0.1	238 ± 10	18.0 ± 0.9
experiments	$E_v=238$	0.5 ± 0.2	238	18.0 ± 0.3
Experiments	none	0.5 ± 0.4	245 ± 10	18.5 ± 0.8
"1"- "4"	$E_v=238$	0.6 ± 0.5	238	17.9 ± 0.2

^aReaction v in reaction schemes 1 - 3 was assumed to govern weight loss. The numbers following the \pm signs in the table are standard deviations.

^bThe fit is given as the average deviation between the calculated and the experimental data in percent of the initial dry sample mass.

The fact that all the linear $T(t)$ experiments could be approximated by the same E_v is connected with the similarity of these TG curves. Figure 1 displays the similarity of the two extreme cases: experiments conducted at 2 and $80^\circ\text{C}/\text{min}$ in helium and argon flows, respectively. The sample size in the latter case was reduced by a factor of 6 to 0.5 mg; nevertheless the highest reaction rates, $(-dm/dt)_{\text{peak}}$ differed by a factor of 5 ($3\mu\text{g}/\text{s}$ vs. $15\mu\text{g}/\text{s}$). Assuming a reaction heat of -320 J/g (Mok and Antal¹⁴) these values correspond to heat consumption peaks of 2.4×10^{-4} and 1.2×10^{-3} J/s, respectively. The effect of the helium flow will be discussed later.

Systematic experimental errors. The variation of the $\log A_v$ values may be due to systematic errors which shift the TG curves along the T axis. The fact that the shape of the curves was not influenced shows that these $_T$ errors, which vary from experiment to experiment, are approximately constant within the decomposition domain of a given experiment. Thermogravimetry, like most other experimental techniques, involves compromises. The majority of the instruments now available are equipped with a thermocouple placed outside of but nearby the sample holder (usually ca. 1 mm below the sample pan). The drawback of this arrangement is that there can be some difference between the temperature of the sample pan and the thermocouple. The advantage is that the thermocouple and its connections do not increase the mechanical inertia of the sample pan; thereby allowing very accurate and sensitive weight measurements. Consequently, the sample masses can be small enough to exclude intra-sample temperature gradients.

Measurements conducted under identical experimental conditions, without altering the position of the thermocouple in the furnace, are reasonably reproducible. (See Figure 2.) However, the reproducibility is worse than in the case of other materials, e.g. carefully prepared mineral coal samples²⁵. The evaluation of the experiments shown in Figure 2 by method (ii) resulted in practically identical $\log (A_v/s^{-1})$ values, 18.09 ± 0.02 .

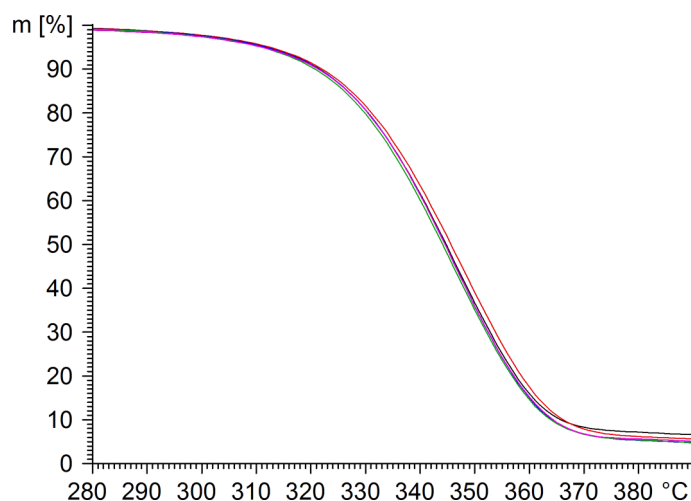


Figure 2. Five TG weight loss curves measured at $10\text{ }^\circ\text{C}/\text{min}$ with strictly identical experimental conditions.

The char yield of the linear $T(t)$ experiments. The mean value and the standard deviation of parameter y_v in the 20 linear $T(t)$ experiments was 0.06 ± 0.01 following either approach (i) or (ii). The results did not show a correlation with heating rate. The original model of Broido does not include a char yield for this reaction. At lower heating rates a small amount of char may be due to the neglected reactions contained in the upper branch of reaction scheme 1. At higher temperatures the probable source

of the chars is secondary cracking of the volatiles, which may depend on the actual size of the grains and their positions within the sample holder.

Evaluation of experiments 1 - 4 at temperatures where the depolymerization reaction dominates. In experiments 1 - 4 we observed that a major part of the decomposition can be described by first order overall kinetics. As will be discussed later, the TG curves in their entirety can only be described by a more complex model. The first order model suffices only in a limited domain consisting of the 40°C/min temperature ramp from the end of the low temperature isothermal section to 370°C and the first few minutes of the 370°C isothermal section. The calculations were carried out by methods (i) and (ii). The results, shown in Table 2, do not differ significantly from the results of the linear $T(t)$ experiments. This fact can be interpreted in such a way that reaction ν in scheme 1 makes a much greater contribution to the mass loss in this domain than the other reactions. It is interesting to note that experiments "3" and "4" represent cases where the original structure of the Avicel sample was probably completely destroyed during the long, low temperature isothermal sections and the remaining unreacted cellulose was contaminated by a large amount of residual solid products. The fits of the model with $E_v = 238$ kJ/mol to the experimental data are shown in Figure 3.

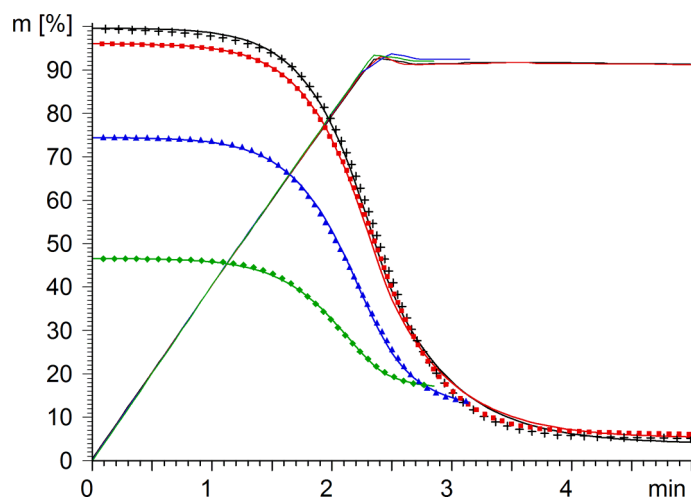


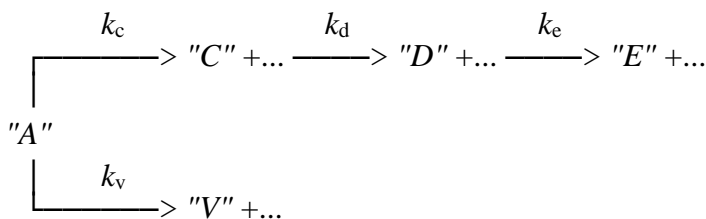
Figure 3. Kinetic evaluation of four non-linear $T(t)$ experiments in selected time domains with $E_v = 238$ kJ/mol. From top to bottom experiments **1** (+++), **2** (■■■), **3** (▲▲▲) and **4** (◆◆◆). (See Table 1). The bold solid lines are the calculated curves resulting from reaction scheme 2 assuming the lower branch (reaction ν) to govern weight loss. The rate constants are displayed in Table 2. The measured $T(t)$ functions are indicated by the thin solid lines which overlap each other. The $t=0$ points were set to correspond to $T=280^\circ\text{C}$.

Qualitative interpretation of char yields from the non-linear $T(t)$ experiments. The amounts of the solid residues observed at various points of the heating programs are shown in Table 1. The data indicate that the Broido-Shafizadeh model is essentially right: there is a competition between processes which result in lower and higher char yields. The $T(t)$ programs having isothermal sections at 260 and 275

°C evidenced a maximum in the final char yield. We note that the maximum char yield at 370 °C displayed in Table 1 (12%) is much less than the comparable yields (17.0-27.6%) reported by Broido and Nelson⁸ for their pretreatment studies. Likewise, Broido and Nelson's char yield without pretreatment (13.1%) is much larger than the char yield we customarily detect (4%). As Broido and Nelson took great care to employ pure cellulose in their work, these gross differences cannot be attributed to the affects of mineral matter on the pyrolysis chemistry. The only plausible explanation is the impact of heterogeneous vapor-solid interactions on char formation (Mok and Antal¹⁴), which would be exaggerated by the large sample sizes emphasized by Broido and Nelson⁸.

Simultaneous evaluation of experiments 2 - 6 in the temperature domain 220 - 370°C. These calculations covered two isothermal sections and two temperature ramps in each curve. A large number of calculations with different initial values of the parameters were carried out to find a model which achieved a good fit to the experimental data. The calculations led to the following conclusions:

(i) The reaction Cellulose → Activated cellulose is either very fast or does not take place at all. In either case it can be omitted from the model. (A more detailed discussion of this conclusion will be given later.) Consequently, the Broido - Shafizadeh model was simplified to



Reaction Scheme 2

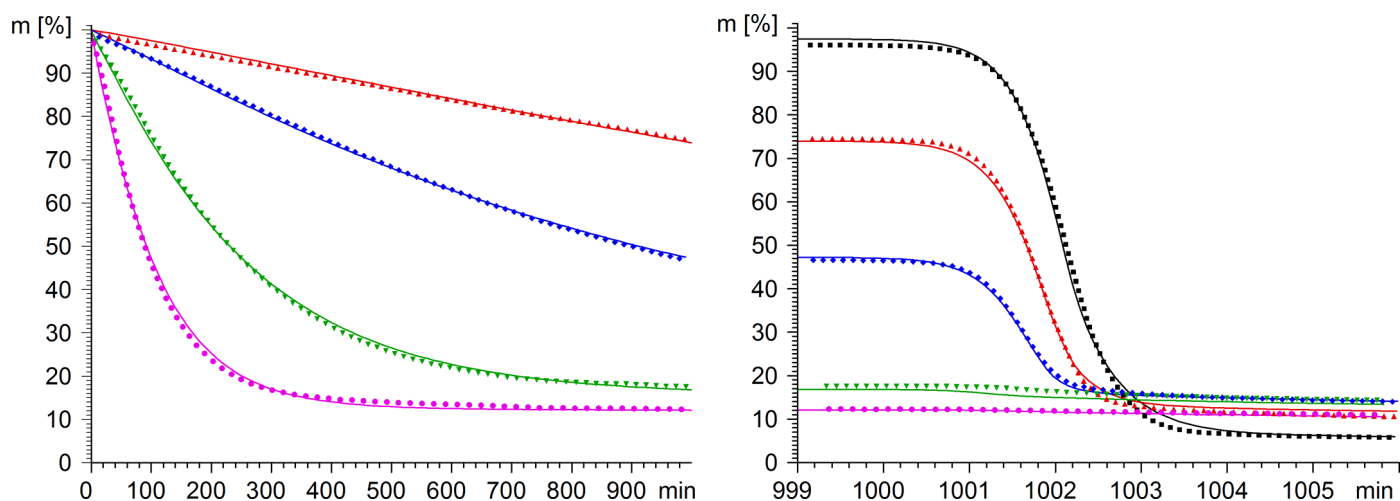
in temperature domain 250 - 370°C. Here "A" is the unreacted cellulose, "C", "D", "E" and "V" denote solid residues and the ellipses represent volatile products.

(ii) The yield of solid residue "V" was found to be zero in all of our calculations, confirming that reaction *v* is really a depolymerization-type reaction.

(iii) Intermediate "D" proved to be a thermally stable compound below 370°C. Hence reaction *e* describes processes taking place during the 370°C isotherms. In this way reaction *e* covers a narrow *T* interval in the model and the value of E_e is not defined uniquely. (A change of E_e could be fully compensated by a suitable change of $\log A_e$ without a significant change in the other parameters or the fit.) Hence a value of $E_e = 250$ kJ/mol was selected more or less arbitrarily and was held fixed during the computation. Note that the original model of Broido and Weinstein⁷ contained only low temperature reactions; consequently reaction *e* differs entirely their reaction 4.

(iv) The value of E_v was taken from Table 2 and was held fixed. In this way the information gathered from the 21 linear $T(t)$ experiments was easily included in the model. As discussed earlier, the corresponding A_v factor evidences a moderate scatter due partly to systematic errors, and partly to side effects resulting from changes occurring in the physical or chemical structure of the unreacted cellulose during the long, low temperature isothermal section. This scattering reflects the slight differences in the decomposition temperatures shown in Figure 3. Hence parameter A_v was allowed to take on different values for the experiments which are the foci of this section.

The "best fit" parameters. The kinetic parameters listed in Table 3 realize a good fit of the model given in scheme 2 to the experimental data. The average fit and its standard deviation is $(0.82 \pm 0.25)\%$. The accord of the model with the data is shown in detail in Figures 4A and 4B. (Since the low temperature sections of experiments 2 and 3 coincided, experiment 2 is displayed only in Figure 4B.) The results show that reaction c dominates in the vicinity of 250°C . Reaction v gradually becomes dominant above 300°C . The $\log A_v$ values (18.1 ± 0.2) fall into the range observed in the linear $T(t)$ experiments (18 ± 0.3) . Reaction e , which describes the decomposition of intermediate "D" around 370°C , is a very slow reaction. At 370°C , k_e is only about $3 \times 10^{-3} \text{ s}^{-1}$.



Figures 4A and 4B. The fit between the calculated and the experimental TG curves assuming reaction scheme 2. Figure 4A and B show the long, low-temperature isothermal sections, and the subsequent ramp till 370°C , respectively. The curves from top to bottom are experiments 2 (■■■, not shown in Fig. 4A), 3 (▲▲▲), 4 (◆◆◆), 5 (▼▼▼) and 6 (●●●). The solid lines represent the calculated curves. (See Tables 1 and 3 for the corresponding $T(t)$ functions and kinetic parameters.)

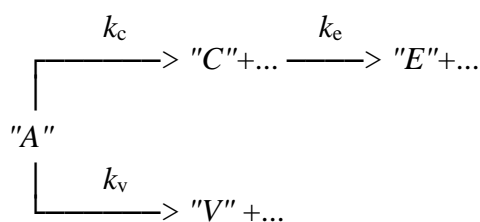
Table 3. Parameters for reaction scheme 2^a

Reaction	E kJ/mol	log (A/s ⁻¹)	y	Rate constants (k/s ⁻¹) at			
				250 °C	290 °C	330 °C	370 °C
c	147	9.5	0.68	8×10 ⁻⁶	8×10 ⁻⁵	7×10 ⁻⁴	4×10 ⁻³
d	174	12.8	0.46	3×10 ⁻⁵	5×10 ⁻⁴	6×10 ⁻³	5×10 ⁻²
e	250	17.7	0.75	6×10 ⁻⁸	3×10 ⁻⁶	1×10 ⁻⁴	3×10 ⁻³
v	238	18.1±0.2	0.00	(2±.9) ×10 ⁻⁶	(1±.4) ×10 ⁻⁴	(3±1) ×10 ⁻³	(6±2) ×10 ⁻²

^alog A_v was allowed to take on different values in the experiments. (See the text for explanation.) The values following the ± signs are standard deviations.

Marked differences exist between the yields displayed in Table 3 and those reported by Broido⁹. In our model $y_c = 0.68$ and $y_d = 0.46$; whereas Broido reported $y_c = y_d = 1.0$. Also, the ultimate potential char yield predicted by the yield parameters given in Table 3 is $0.68 \times 0.46 \times 0.75 = 0.235$; whereas Broido reported an ultimate yield of 0.321. We attribute this difference to the large samples employed by Broido and his co-workers, which engendered char formation via secondary reactions between the volatile species and the decomposing solid. This enhancement of char formation would manifest itself as artificially large values of the yield parameters.

Arseneau's reaction scheme supplemented with a reaction for the 370 °C region. The data given in Table 3 show that reaction *c* is essentially rate determining in the low temperature region. This result suggests that reaction *d* may not be required in the model. A reaction scheme consisting of only reactions *c* and *v* was proposed by Arseneau²⁶. He found activation energies $E_c = 152$ and $E_v = 190$ kJ/mol. Bradbury, Sakai and Shafizadeh¹⁰ used the same model to determine the parameters of reactions *c* and *v* in their work. (They determined E_c , A_c , E_v and A_v from differential equations which actually corresponded to the Arseneau's model and obtained the parameters of the *cellulose* → *active cellulose* step by another method.) They found similar activation energies: $E_c = 150$ and $E_v = 198$ kJ/mol with preexponential factors $\log (A_c/s^{-1}) = 10.1$ and $\log (A_v/s^{-1}) = 14.5$. We added reaction *e* (which describes the decomposition of intermediate "C" at higher temperatures) to Arseneau's scheme:

*Reaction Scheme 3*

and studied the ability of this new, simplified model to mimic the data. Although the fits were acceptable, they were less good than those of scheme 2: the average deviations between the calculated and the simulated data were about 1.2 times larger. The "best fit" parameters are listed in Table 4. Note that the parameters associated with reaction *c* are quite close to the ones reported by earlier workers^{10,26}. It is interesting to observe that the first lines of Tables 2 and 3 are practically identical; hence the inclusion or omission of reaction *d* does not influence these values. (The actual difference between the E_c and $\log A_c$ values of the two tables is 0.26 and 0.10, respectively.) This result indicates that the parameters of reaction *c* are very well defined, and their determination is not sensitive to the experimental techniques or the mathematical methods employed. Note that at low temperatures the decomposition is so slow that heat transfer limitations do not impact on results. As mentioned earlier, the parameters of reaction *v* reported by Bradbury¹⁰ et al. are probably compromised by heat transfer intrusions associated with the large sample masses employed in their higher temperature, isothermal experiments.

Table 4. Parameters for reaction scheme 3^a

Reaction	E kJ/mol	$\log(A/s^{-1})$	y	Rate constants (k/s^{-1}) at			
				250°C	290°C	330°C	370°C
c	147	9.4	0.37	6×10^{-6}	3×10^{-5}	5×10^{-4}	3×10^{-3}
e	250	17.5	0.76	4×10^{-8}	2×10^{-6}	8×10^{-5}	2×10^{-3}
v	238	18.1 ± 0.2	0.00	$(2 \pm 1) \times 10^{-6}$	$(1 \pm .5) \times 10^{-4}$	$(3 \pm 1) \times 10^{-3}$	$(6 \pm 3) \times 10^{-2}$

^a $\log A_v$ was allowed to take on different values in the experiments. (See the text for explanation.) The values following the \pm signs are standard deviations.

Concerning the cellulose \rightarrow active cellulose reaction. When we evaluated scheme 1, rate constant k_b tended to infinity, indicating that this reaction either does not take place at all, or it occurs only at lower temperatures. During the evaluation, we found some intermediate sets of parameters which gave an acceptable fit to the data, but the fit without the assumption of this reaction was the best.

When we added the cellulose \rightarrow active cellulose reaction to reaction scheme 3, i.e. when we supplemented the Broido - Shafizadeh model with a 370°C reaction, we were unable to find any sets of parameters which resulted in a reasonable fit. When the char yield of this reaction, y_b was allowed to vary, a local minimum was found at $E_b = 203$ kJ/mol, $\log(A_b/s^{-1}) = 15.2$ and $y_b = 0.5$ (!). Since the formation of 50 % volatiles seemed meaningless in reaction *b*, and the fit was worse than that offered by models which did not include reaction *b*, this parameter set was rejected.

Finally the question arose: "Can we improve upon scheme 2 by including more steps/parameters into the model?" (ie. "Is there any reason to look for better fits than those shown in figures 4A and 4B?")

Keeping in mind the extraordinary changes in the physical structure of the sample, which must occur as the cellulose decomposes and the solid intermediates are formed, one cannot require a fit which incorporates the finest details of the experimental curves using only a simplified model consisting of a few first order reactions.

Thermogravimetry - Mass Spectrometry. In an earlier study¹⁶ we reported simultaneous TG-MS studies of Avicel decomposition at linear heating programs of 10 and 80°C. In this work we conducted an additional experiment with the same equipment to identify the gaseous decomposition products formed during the heating of a low temperature solid residue to higher temperatures. We were unable to monitor the low temperature sections themselves, since the connection between the balance and the mass-spectrometer¹⁶ was designed for overall reaction rates of $-dm/dt \sim 1 - 100 \mu\text{g/s}$. The $T(t)$ program of this experiment consisted of an isothermal section of 46 hours at 250°C followed by a 10°C/min temperature ramp. The other experimental conditions were identical to the TG-only experiments described earlier. We observed the same mass spectrometric fragment ions as in our previous work, although their ratios differed in the various sections of the curve. It is interesting to note that glycolaldehyde (hydroxyacetaldehyde), which is a major product of the pyrolysis of larger samples of cellulose³⁻⁵, was detected only in trace amounts in the present work, as was the case in our earlier research¹⁶. This finding supports the view that glycolaldehyde is formed by secondary reactions of the volatile species, as stated by Piskorz et al³.

Effects of a helium gas purge. High molecular weight volatiles have ca. 3 times higher diffusion coefficients in helium than in argon; hence the use of helium is an ideal tool to check the role of secondary reactions in atmospheric pressure experiments. Unfortunately, the results of the helium and argon experiments cannot be compared directly since helium has ca. 8 times better heat conductivity than argon; hence the temperature distribution in the furnace and the temperature difference between the sample holder and the thermocouple is different in the two cases. A qualitative comparison of experiments 4 and *H* revealed striking similarities. However, experiment *H* appeared to evidence slightly higher reaction rates at identical, measured temperature values. Seeking a more quantitative evaluation, we used the parameter values obtained from the argon experiments with reaction scheme 2 to model experiment H. As in the other calculations, $\log A_v$ was allowed vary. The other parameters were treated as constants. To describe the expected thermal differences between the argon and the helium experiments, an additional $_T$ parameter was defined. The integration of the ODE system was carried out at $T(t) = T^{\text{exper}}(t) + _T$, where $T^{\text{exper}}(t)$ is the temperature measured by the thermocouple. The calculation resulted a fit of 0.6 %, which is better than the average value of the argon experiments (0.8%), with $_T = 1.1 \text{ }^\circ\text{C}$. This value can probably be accepted as a rough estimate of the temperature difference between the thermocouple and the sample pan in the isothermal sections of the experiments. The value of $\log (A_v/s^{-1})$

was found to be 18.3, which is higher than the value associated with experiment 4 (18.1), but still within the range of A_v values obtained from the argon experiments (18.1 ± 0.2).

In the linear $T(t)$ helium experiments there was no need to use a similar procedure since a variation in $\log A_v$ can formally compensate for nearly constant temperature differences. The three helium experiments resulted in average $\log (A_v/s^{-1})$ and fit values of 18.1 and 0.47 %, respectively, which fall in the range calculated from all of the 21 linear $T(t)$ experiments: 18.0 ± 0.2 and $(0.52 \pm 0.23)\%$.

CONCLUSIONS

1. The *cellulose* \rightarrow *active cellulose* step of the Broido-Shafizadeh model is superfluous within the temperature range 250°C - 370°C. Experimental results are better represented by models which exclude this reaction.

2. A modified Broido-Shafizadeh type model (Scheme 2) which omits an initiation reaction, but includes a high temperature (370 °C) decomposition step (not mentioned in the work of Broido or Shafizadeh), achieves an excellent fit to all the experimental data reported in this paper.

3. Char yields reported in this work are much lower than those measured by Broido and his colleagues. This difference seems to be a result of the large samples employed by Broido, which enhanced the pyrolytic vapor-solid interactions that led to char formation.

4. Reaction scheme 3, which is Arseneau's model²⁶ supplemented with the high temperature reaction mentioned above, achieves a good fit to the experimental data.

5. Complicated models, which possess more than one reaction step, are not needed to simulate the weight loss behavior of cellulose heated continuously at a rate of 2 °C/min or more. Under these conditions, the depolymerization step included in the models mentioned above is rate limiting. Consequently, a first order, single step model with a high activation energy ($E_v = 238$ kJ/mol) is able to accurately mimic weight loss data at heating rates of 2 °C/min or more.

6. The kinetic parameters of the depolymerization reaction remain essentially unchanged even after the sample has suffered 16 hours of decomposition at temperatures between 250 and 280 °C, and the unreacted cellulose is contaminated by a large amount of organic solid decomposition products. This result indicates that cellulose decomposition is probably not sensitive to the physical structure of the sample. We note that this finding is in good accord with earlier work that details the pyrolysis kinetics of a wide variety of cellulose samples, and the cellulose components of various herbaceous biomass samples which were freed of mineral matter by acid washing or hot water washing procedures²³.

7. Finally we wish to emphasize that these results are relevant to the decomposition of ash-free cellulose under experimental conditions which almost completely exclude secondary reactions. The effects of mineral matter and secondary reactions on the kinetics of cellulose decomposition have been discussed in earlier publications^{21,27}.

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