Thermal Degradation of Cellulose in Air and Nitrogen at Low Temperatures

F. SHAFIZADEH and A. G. W. BRADBURY, *Wood Chemistry Laboratory, Department of Chemistry, University of Montana, Missoula, Montana 59812*

Synopsis

Thermal analysis and kinetic studies have shown that oxidative reactions are responsible for acceleration in the rates of weight loss and depolymerization of cellulose on pyrolysis in air at temperatures below 300°C. The oxidative reactions include production of hydroperoxide, carbonyl, and carboxyl groups, which have been investigated at lower temperatures along with the rates of depolymerization and production of carbon monoxide and carbon dioxide. The experimental results are consistent with an autoxidation mechanism involving initiation, propagation, and decomposition reactions. At temperatures above 300°C, the rate of pyrolysis is essentially the same in both air and nitrogen, indicating that thermal degradation is independent of the oxidative reactions.

Introduction

The ability of atmospheric oxygen to enhance degradation of cellulose at lower temperatures is well known.[1] It is also known that autoxidation reactions are strongly influenced by impurities or additives in the substrate. This factor is undoubtedly responsible for the large variation in rate constants and activation energies obtained for autoxidative degradation of cellulose or cellulose containing materials.[2]

In view of the significance of oxidative degradation in smoldering combustion and autoignition, we have investigated the effect of oxidative conditions on the thermal degradation rates of purified cellulose to determine the kinetics and mechanisms of the reactions involved.

EXPERIMENTAL

Cotton cellulose linters were extracted with fresh batches of boiling ethanol over 2 days and then soaked 3 times in 80°C water for 1-hr periods. A sample of the purified material showed a DP (degree of polymerization) of 2530.

Thermal analysis was carried out with the methods and equipment described previously.[3] In the isothermal experiments, samples were placed on the thermobalance and rapidly heated to the desired temperature. In the temperature range of 275–325°C, the initial heating period required about 1 min and was allowed for by extrapolation.

In the experiments carried out at lower temperatures, cotton samples (0.2 g) were heated in an aluminum boat inside a glass pyrolysis tube (diameter 4.5 cm). The temperature profile of the sample was determined by using three thermocouples and found to be constant in the temperature range of 150–190°C.

Gas flows were at the rate of 60 ml/min. Air currents were first passed through

sodium hydroxide solution and anhydrous calcium sulfate. For studies in nitrogen, oxygen was carefully excluded by evacuating the pyrolysis tube before introducing the inert gas. The sample was then moved into the reaction zone by use of a magnet and required about a minute to reach the reaction temperature. For any given period the samples were heated continuously.

The *DP* was determined by nitration and viscometry according to the method of Alexander and Mitchell[4] using a modified Ubbelohde viscometer and acetone as solvent. *DP*s were obtained by multiplying the intrinsic viscosity by 94. Kjeldahl analysis[5] showed nitrogen contents of $13.6 \pm 0.3\%$ for selected cellulose nitrates; eliminating the necessity of correction for incomplete nitration.

Carbon dioxide was analyzed by passing the pyrolysis gases into two barium hydroxide absorption flasks (100 ml, $0.005M$) and titrating the excess barium hydroxide with dilute hydrochloric acid ($0.04M$). Carbon monoxide was converted to carbon dioxide by passing the effluent gas through iodine pentoxide at 130°C, and analyzed as above.[6]

Carboxyl groups were determined by absorption of the cationic dye, methylene blue.[7] The relative number of free carboxyl and lactonized carboxyls was determined by repeating the analysis following borohydride reduction.

Aldehyde groups were determined by the difference in methylene blue absorption before and after treatment with sodium chlorite.[8] This method was preferred to the "copper-number" method, which did not give reproducible results at these low degrees of substitution.

Carbonyl groups were determined by conversion to cyanohydrins and titration of excess sodium cyanide with silver nitrate.[9] This method gives the total number of ketone and aldehyde groups. The ketone groups were calculated by difference.

An iodometric method[10] was used to estimate hydroperoxide content. The reaction was carried out in freshly distilled isopropyl alcohol to prevent air oxidation. Results were checked with an alternative colorimetric method whereby phenolphthalin was oxidized to phenolphthalein by hydroperoxide.[11]

Oxycellulose containing carboxyl end groups was obtained by oxidizing hydrocellulose[12] with sodium chlorite. Oxycellulose with carboxyl groups at C2 and C3 was obtained by similar oxidation of a periodate oxidized cellulose.[13] Treatment of cellulose with nitrogen dioxide[14] gave an oxycellulose containing carboxyl groups predominantly at C6.

RESULTS AND DISCUSSION

Rates of Degradation

Thermal analysis of cellulose heated dynamically at a rate of 15°C/min reveals distinct differences between oxidative and inert conditions (Fig. 1). The maximum rate of weight loss occurs at 345°C in air and 360°C in nitrogen. DTA (differential thermal analysis) in air shows an exothermic reaction beginning at 270°C and ending at ~400°C. This exotherm is interrupted by an endotherm, centered at ~330°C. The endotherm can be attributed to formation and evaporation of volatile pyrolysis products, and the exotherm is due to the oxidation of these products. Another exotherm, peaking at 490°C, represents oxidation of the charred residue. In nitrogen, there is only a large endotherm,
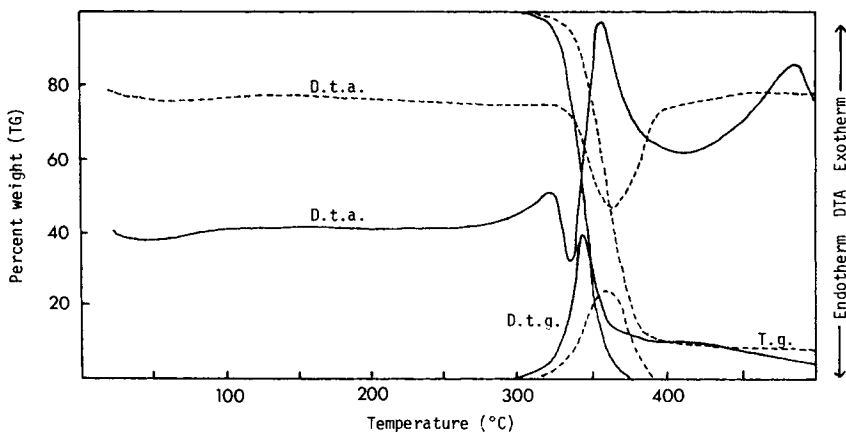
Fig. 1. Thermal analysis of cellulose heated in air (—) and nitrogen (- - -).

starting at $\sim 300°$C, which corresponds to the weight loss caused by production and evaporation of volatile products.

The initial oxidative degradation of cellulose in air could be seen more clearly in Figure 2, which gives the rates of weight loss under isothermal conditions in the temperature range of 275–325°C. In this figure the log of the normalized weight ($W - W_\infty/W_0 - W_\infty$, where W is the weight at time t, W_0 is the initial weight, and W_∞ is the final residue weight) is plotted against time t. Up to 310°C, these plots show an initiation period before following a first-order reaction. The initiation period is diminished with increasing temperature and disappears at temperatures above 310°C, where the plots for the oxidative and inert atmospheres are superimposed. The Arrhenius plot for the first-order rate constants (Fig. 3) shows a divergence in the slopes of the plots, which come to-
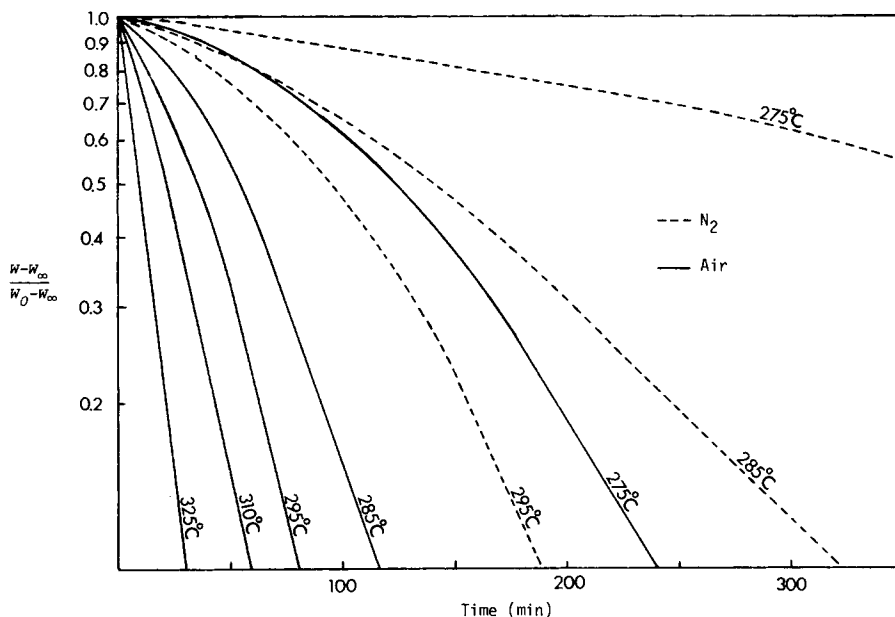

Fig. 2. First order plot for the residual cellulose weight (normalized) versus time. Plots at 310°C and 325°C for air and nitrogen are similar.
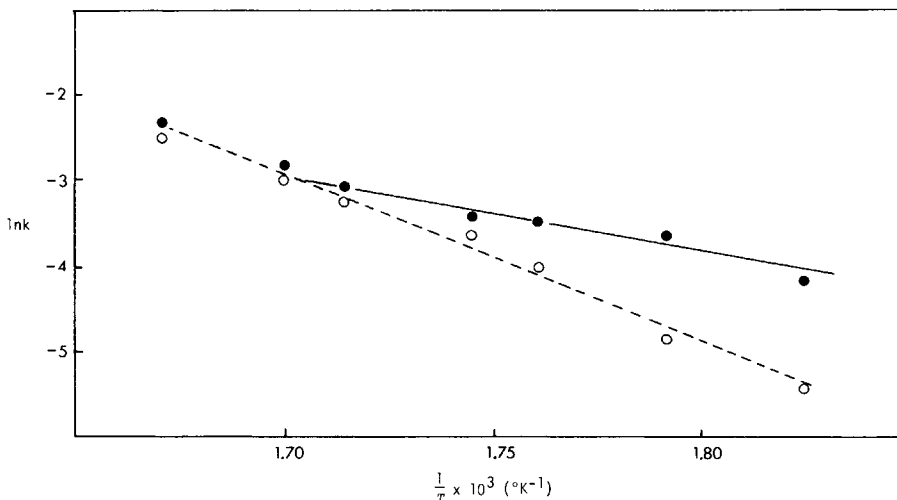
Fig. 3. Arrhenius plot for the first order reaction in the isothermal degradation of cellulose in air (—) and nitrogen (- - -).

gether at 310°C. Values of activation energy E are 17 kcal/mole in air and 37 kcal/mole in nitrogen. The value in nitrogen compares favorably with other literature values.[1,15,16]

To gain further information about the initial pyrolytic reactions, it was decided to investigate the rate of depolymerization. A lower temperature range was selected for this investigation in order to minimize (1) the effect of uneven heat transfer in the larger samples required and (2) reaction during the warmup period before the isothermal condition is reached.

Figure 4 gives value of P_v (viscosity-average DP) as a function of time for samples heated isothermally in air within the range of 150–190°C. To a good approximation, P_v is equal to P_w (weight-average DP).[17] For a polymer of random distribution (a good approximation for cellulose), P_w is about twice that of P_n (number-average DP).[18] That is,

$$P_v = P_w = 2P_n \tag{1}$$

The total number of bonds in the polymer (x) at any time is given by

$$x = N - N/P_n \tag{2}$$

where N is total number of monomeric units in the system. The rate of chain scission is given by

$$dx/dt = -kx^a \tag{3}$$

where a is the order of reaction. If $a = 0$, following integration,

$$x_0 - x_t = k(t_0 - t) \tag{4}$$

or

$$1/P_{n(t)} - 1/P_{n(0)} = k_0 t \tag{5}$$

where $P_{n(0)}$ and $P_{n(t)}$ is the DP at zero time and time t, respectively, and k_0 is a zero-order rate constant.
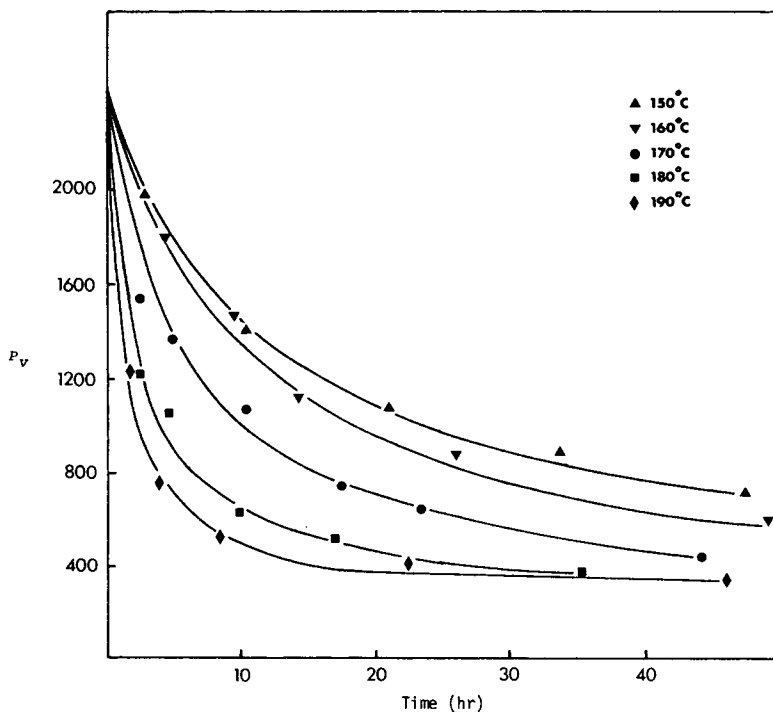
If $a = 1$, then

Fig. 4. Viscosity average degree of polymerization (P_v) of cellulose heated in air at 150°C–190°C.

$$\ln x - \ln x_t = kt \text{ or } \ln\left(1 - \frac{1}{P_{n(0)}}\right) - \ln\left(1 - \frac{1}{P_{n(t)}}\right) = k_1 t \qquad (6)$$

At large values of P_n, this equation simplifies to eq. (5) above.

Thus, as pointed out by McBurney,[17] a first-order bond-scission reaction follows zero-order kinetics at the initial stages of degradation. Consequently, the term order of reaction is ambiguous as applied to the initial random degradation of polymer.

Plots of $1/P_{n(t)}$ against t are shown in Figure 5 for the cotton samples in air and nitrogen between 150 and 190°C. An initial small deviation (possibly due to some weak links) is followed by a linear portion, indicating random bond scission, and then a slackening off in the rate of P_n decrease beginning at $P_n \simeq 250$, corresponding to $P_w = 500$. Assuming that the rate of chain scission is constant, this deviation from linearity indicates a decreasing P_w/P_n ratio. This means that in the last stage the chain scission is less random and a levelling-off DP is being approached.

Samples heated at 170°C and above for longer periods than those shown here were partially insoluble following nitration. Application of sodium borohydride before nitration did not improve solubility. However, a P_w of 160 was estimated for the 40% soluble portion of a sample that had been heated at 170°C in air for 200 hr. The levelling-off DP value is encountered in both thermal degradation and acid hydrolysis studies. For the former, values of [19] 190 and [20] 200 have been claimed, whereas various values ranging from 150 to 200 have been estimated for the latter. We obtained a DP of 170 for cotton cellulose that had been treated with constant boiling hydrochloric acid at its boiling temperature for 2 min.
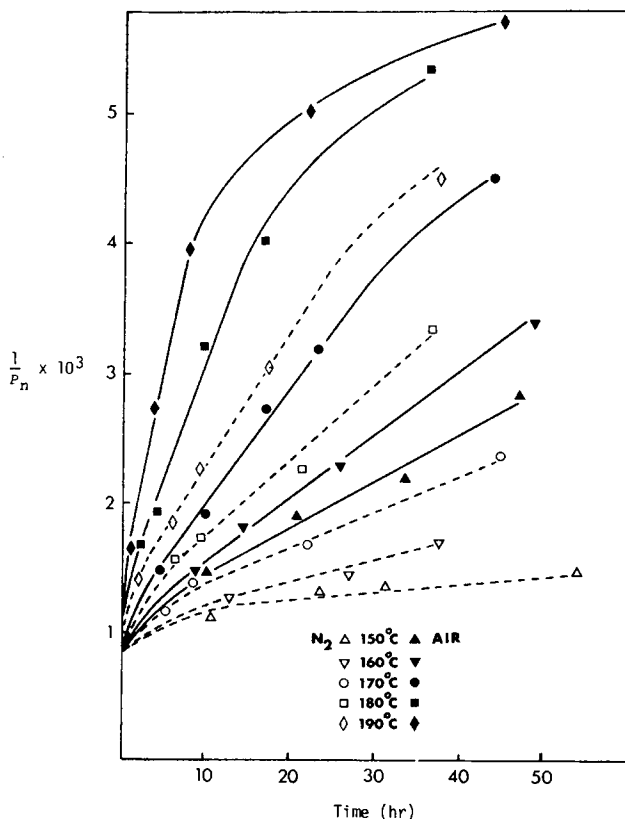
Fig. 5. Reciprocal of number average degree of polymerization (P_n) vs time for cellulose heated in air and nitrogen at 150°C–190°C.

The rate constants for bond scission calculated from the straight lines in Figure 5 by application of eq. (5) are shown in Table I. Arrhenius plots for these rate constants shown in Figure 6 gave activation energy values of 21 kcal/mole for bond scission in air and 27 kcal/mole in nitrogen. The latter result compares favorably with the value of 25.8 kcal/mole found in the literature for depolymerization in the absence of air,[21] but is somewhat lower than the value of 35.4 kcal/mole given for depolymerization in vacuum.[22]

This data indicates that at lower temperatures a relatively larger number of bonds are broken under oxidative conditions than in nitrogen; however, as the

TABLE I
Rate Constants for the Depolymerization of Cellulose in Air and Nitrogen

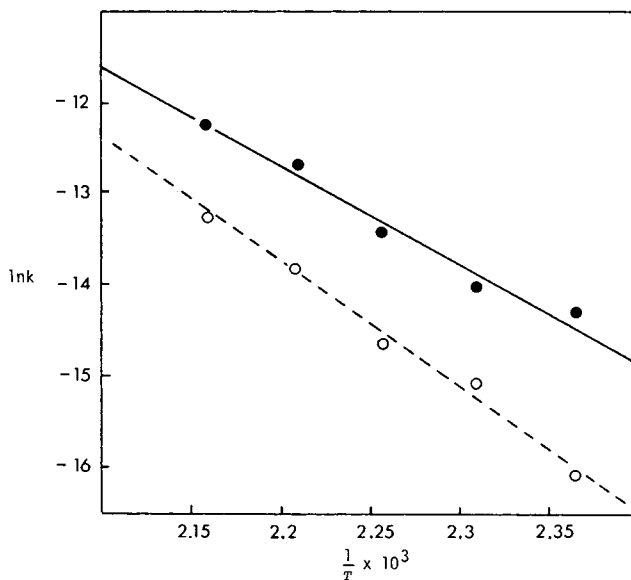| Temperature,°C	$k_0 \times 10^7$ in N_2 mole/162 g min[a]	$k_0 \times 10^7$ in Air mole/162 g min
150	1.1	6.0
160	2.8	8.1
170	4.4	15.0
180	9.8	29.8
190	17.0	48.9

[a] 162g represents 1 mole of monomer unit.

Fig. 6. Arrhenius plot for the rate of bond scission in air (—) and nitrogen (- - -).

temperature increases this difference gradually disappears. For example, it can be estimated that at 25°C, in air, 7.8×10^9 bonds/min/g cellulose are cleaved. Whereas at the same temperature in nitrogen, 1.7×10^8 bonds are cleaved, or 45 times less.

Chemical Reactions

Figure 7 shows the rate of production of carbon monoxide and carbon dioxide at 170°C in air and in nitrogen. The rate of evolution of these gases is much faster in air than in nitrogen and, furthermore, accelerates on continued heating. It is constructive to compare the initial linear rates for the emission of these gases
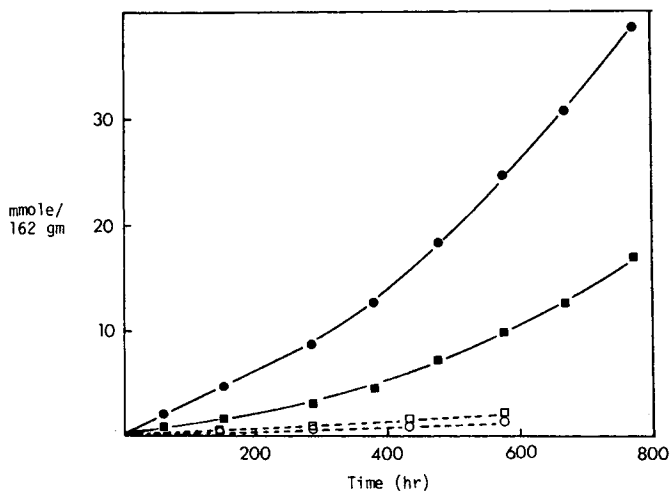

Fig. 7. Yields of CO and CO_2 from heating cellulose at 170°C: (O)CO_2 in N_2; (□)CO in N_2; (●)CO_2 in air; (■)CO in air.

TABLE II
Initial Rates of Glycosidic Bond Scission and Carbon Monoxide and Carbon Dioxide Formation
at 170 °C

Reaction	Rate $\times 10^5$ in N_2, mole/162 g hr	Rate $\times 10^5$ in Air, mole/162 g hr
Bond scission[a]	2.7	9.0
CO evolution[b]	0.6	2.1
CO_2 evolution[b]	0.4	6.4

[a] Calculated from the rate constants in Table I.
[b] Calculated from initial linear portion of plots in Figure 8.

with the rates of bond scission obtained for depolymerization at 170°C, discussed before. As can be seen in Table II, for air the rate of bond scission approximately equals the rate of production of carbon dioxide plus carbon monoxide in moles per glucose unit. In nitrogen, however, the rate of bond scission is greater than the combined rates of carbon monoxide and carbon dioxide evolution.

It is assumed that carbon dioxide and carbon monoxide may be formed by decarboxylation and decarbonylation, respectively, as well as by other competing reactions. The significance of the former reactions was determined by measuring the net rate of accumulation of carboxyl and carbonyl groups in cellulose on heating in air at 190°C. The results shown in Fig. 8 indicate an almost linear rate of formation on heating for 50 hr. On heating for longer periods, the rate of accumulation of carboxyl groups falls off, and the rate of accumulation of aldehyde groups is increased. The latter effect, however, could be due to the sodium chlorite method employed for the oxidation and measurement of the aldehyde groups. These data show the production of carboxylic and aldehyde
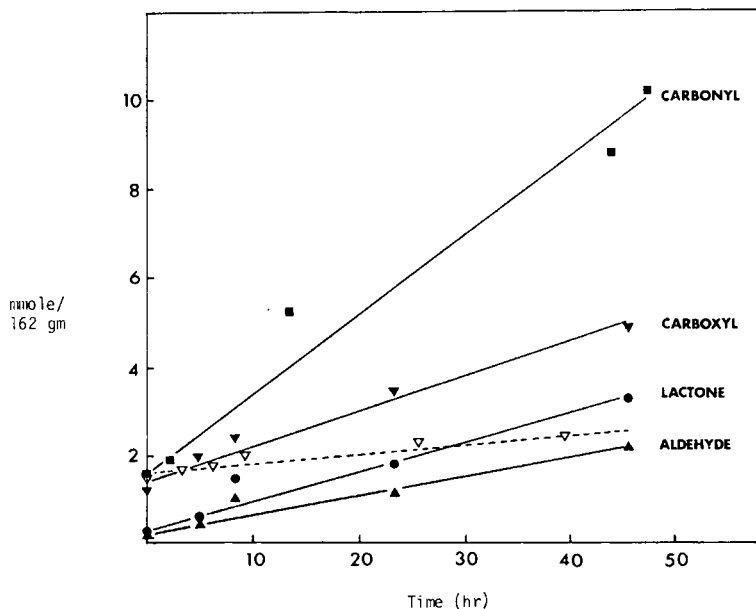

Fig. 8. Incorporation of oxidized groups in cellulose at 190°C - - - - ▽ - - - represents number of lactone and carboxyl groups formed in nitrogen at 190°C.

groups on oxidation of cellulose in air. There was also a very small increase in the number of oxidized functions on heating in nitrogen. In order to check the extent of decarboxylation at the relatively lower pyrolysis temperatures, samples of low-DS (degree of substitution) carboxylcellulose with carboxyl groups at C1, C2 and C3, and C6 were prepared and pyrolyzed. The results shown in Figure 9 are, by and large, inconclusive, except for the sample oxidized at C2 and C3, which showed a definite reduction in carboxyl-group content. Thus, although both carboxyl and carbonyl groups, as well as carbon dioxide and carbon monoxide, are formed during low-temperature pyrolysis, the production of the latter compounds could not be directly related to the formation of the former functions.

The thermal degradation of cellulose in air, similar to that of synthetic polymers,[23] may involve a free-radical mechanism. We were not able to observe these radicals, but were able to monitor the formation of hydroperoxide groups on heating cellulose in air. The hydroperoxide functions are simultaneously formed and decomposed, and their concentration rapidly climbs until a steady state is reached. Figure 10 shows the development of the steady-state concentration in air at 170°C during a period of about 100 min. It also shows the rate of decay in nitrogen over a similar period. This decay of the hydroperoxide function appeared to follow first-order kinetics with a rate constant of 2.5×10^{-2} min^{-1} at 170°C. From the steady-state concentration of 3.0×10^{-5} mole/162 g, the rate of hydroperoxide decomposition is thus 7.5×10^{-7} mole/162 g min. When compared with the initial rate of bond scission in air of 1.5×10^{-6} mole/162 g min at 170°C (Table I), it is apparent that the hydroperoxide formation could make a significant contribution to bond scission.
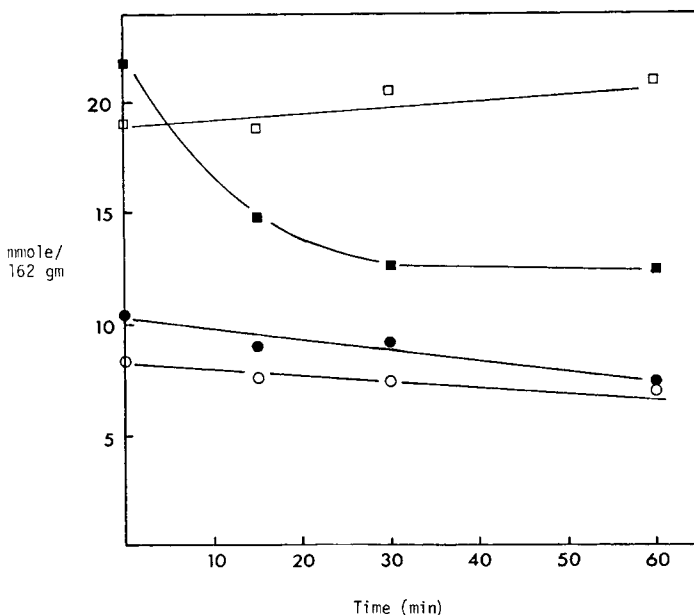

Fig. 9. Effect of heating on carboxyl content of carboxyl celluloses in nitrogen at 190°C. (O) 1-carboxyl cellulose; (■) 2,3-carboxyl cellulose; (□) 6-carboxyl cellulose; (●) prepared by heating cellulose in air at 190°C.
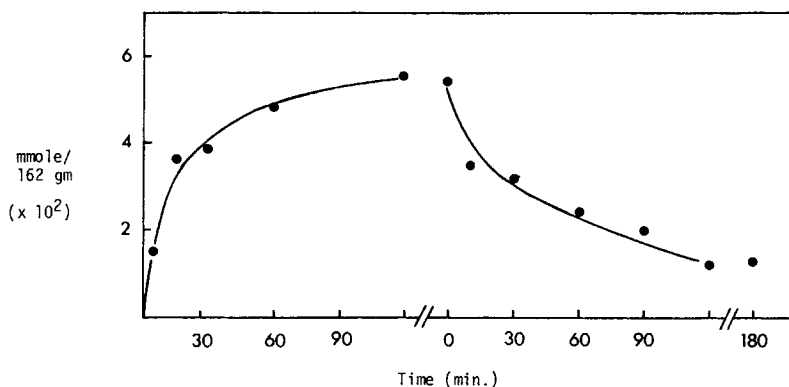
Fig. 10. Rate of formation and decay of hydroperoxide groups in cellulose at 170°C. Formation is in air and decay is in nitrogen.
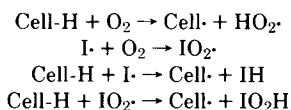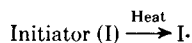
CONCLUSIONS

Thermal degradation of cellulose is a first-order reaction at high temperatures. At lower temperatures there is an initiation period that is prolonged as temperature is lowered, whereas the first-order reaction is shortened. At higher temperatures, pyrolysis proceeds rapidly via transglycosylation reactions leading to anhydro sugars as the principal thermolysis products.[1,3] These processes overshadow the effect of oxygen or an oxidative environment, whereas at lower temperatures, oxygen plays a dominant role and oxidative degradation progressively proceeds faster than pyrolysis in nitrogen. The initiation period of the low-temperature reaction involves the production of free-radical initiators.

These initiators can arise from (1) thermal action on trace quantities of impurities, (2) the action of oxygen with a substance other than substrate[24] or (3) from direct hydrogen abstraction by oxygen (a highly endothermic reaction, and less likely).[24] Subsequent interaction of these initiators with oxygen can lead to thermal autoxidative reactions characteristic of general polymers.[23,25] Thus low-temperature oxidation can be envisaged as proceeding in three stages: initiation, propagation, and production of degradation products (Scheme I). Reaction propagation is via the production of hydroperoxides that quickly reach a steady-state concentration at low temperatures.
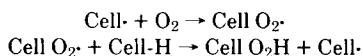
Products of reaction include carboxyl and carbonyl groups that are incorporated in the cellulose. The rates of production of carbon dioxide and carbon monoxide gradually accelerate, indicating the autocatalytic nature of the reaction.

Analogous to radiation studies of cellobiose[26] and autoxidation studies of methyl β-D-glucopyranoside,[27] H-abstraction (by peroxy radical, ROO·) could be expected to take place dominantly at C1. Subsequent oxygen addition and hydrogen abstraction leads to a further hydroperoxide function, which in view of the first-order decay, could split homolytically to give an alkoxy radical and a hydroxy radical (a further H abstractor). A β-scission could then result in cleavage of the glycosidic bond and an alkoxy radical on the neighboring glucose unit. This postulated mechanism of oxidative bond scission is shown in Scheme II.
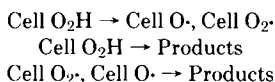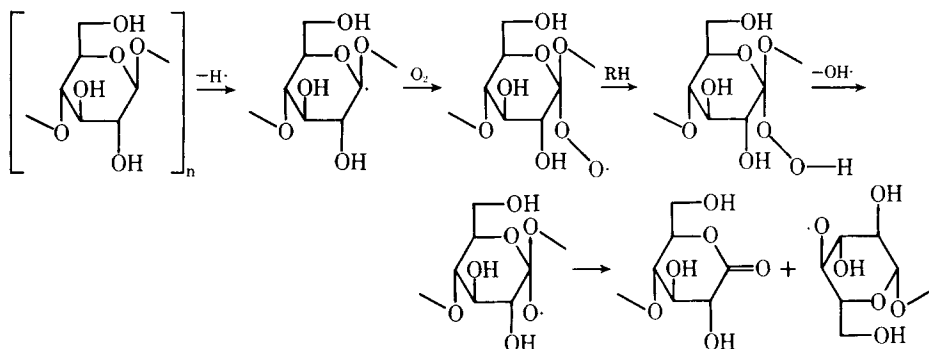
Initiation

$$\text{Initiator (I)} \xrightarrow{\text{Heat}} \text{I} \cdot$$

$$\text{Cell-H} + O_2 \rightarrow \text{Cell} \cdot + HO_2 \cdot$$
$$\text{I} \cdot + O_2 \rightarrow IO_2 \cdot$$
$$\text{Cell-H} + \text{I} \cdot \rightarrow \text{Cell} \cdot + IH$$
$$\text{Cell-H} + IO_2 \cdot \rightarrow \text{Cell} \cdot + IO_2H$$

Propagation

$$\text{Cell} \cdot + O_2 \rightarrow \text{Cell } O_2 \cdot$$
$$\text{Cell } O_2 \cdot + \text{Cell-H} \rightarrow \text{Cell } O_2H + \text{Cell} \cdot$$

Formation of Products

$$\text{Cell } O_2H \rightarrow \text{Cell } O \cdot, \text{Cell } O_2 \cdot$$
$$\text{Cell } O_2H \rightarrow \text{Products}$$
$$\text{Cell } O_2 \cdot, \text{Cell } O \cdot \rightarrow \text{Products}$$

Scheme I. The thermal autoxidation of cellulose in air.

Scheme II. Possible mechanism of formation and decomposition of cellulose hydroperoxide in air.

Oxidation of the volatile products, indicated by the appearance of an exotherm during the pyrolysis of cellulose, could also be responsible for the accelerated rate of decomposition of the solid substrate in air shown by the thermal analysis and kinetic data (see Figs. 1–4, 7). This means that thermal decomposition in the solid phase could be accelerated by the free-radical species produced during the combustion in the gas phase.[28]

As shown in Figure 7, carbon monoxide and carbon dioxide are also formed under nonoxidative conditions at 170°C. A possible source of these products could be the glycosyl free radical produced on abstraction of H at position 1, (Scheme II). These radicals could undergo rearrangement through an unsaturated intermediate and addition of water to give carboxylic acid or lactone functions, which decarboxylate or decarbonylate (as shown in previous publications in this series[29–31]).

References

1. F. Shafizadeh, *Adv. Carbohydr. Chem.*, **23**, 419 (1968).

2. I. K. Walker, W. J. Harrison, and G. F. Paterson, *N.Z. J. Sci.*, **17**, 271 (1976).

3. F. Shafizadeh, R. A. Susott, and G. D. McGinnis, *Carbohydr. Res.*, **22**, 63 (1972); F. Shafizadeh and Y. L. Fu, *Carbohydr. Res.*, **31**, 57 (1973).

4. W. J. Alexander and R. L. Mitchell, *Anal. Chem.*, **21**, 1497 (1969).

5. J. W. Green, *Methods Carbohydr. Chem.*, **3**, 229 (1963).

6. M. Steinberg, A. Glasner, and E. Levy, *Anal. Chem.*, **34**, 1629 (1962).

7. G. F. Davidson and T. P. Nevell, *J. Text. Inst.*, **39**, T59 (1948).

8. M. Pasteka, *Methods Carbohydr. Chem.*, **6**, 85 (1972).

9. M. Lewin, *Methods Carbohydr. Chem.*, **6**, 76 (1972).

10. R. D. Mair and A. J. Graupner, *Anal. Chem.*, **36**, 194 (1964).

11. L. M. Maraccini and T. N. Kleinert, *Svensk Papperstid.*, **65**, 78 (1962).

12. J. F. Saeman and M. A. Millett, *Methods Carbohydr. Chem.*, **3**, 131 (1963).

13. T. P. Nevell, *Methods Carbohydr. Chem.*, **3**, 164 (1963).

14. T. P. Nevell, *J. Text. Inst.*, **42**, T91 (1951).

15. A. E. Lipska and W. J. Parker, *J. Appl. Polym. Sci.*, **10**, 1439 (1966).

16. P. K. Chatterjee and C. M. Conrad, *Text. Res. J.*, **36**, 487 (1966).

17. L. F. McBurney, *Cellulose and Cellulose Derivatives*, E. Ott, H. M. Spurlin, and M. W. Grafflin, Eds., Interscience, New York, 1954, Part 1, pp. 108–112.

18. P. J. Flory, *J. Am. Chem. Soc.*, **58**, 1877 (1936).

19. O. P. Golova, *Usp. Khim.*, **44**, 1454 (1975).

20. W. D. Major, *Tappi*, **41**, 530 (1958).

21. A. Pacault and G. Sauret, *Compt. Rend Acad. Sci.*, **246**, 608 (1958).

22. D. P. C. Fung, *Tappi*, **52**, 319 (1969).

23. J. F. Rabek, *Comprehensive Chemical Kinetics, Vol. 14, Degradation of Polymers*, C. H. Bamford and C. F. H. Tipper, Eds., Elsevier, New York, 1975, pp. 476–481.

24. N. Uri, *Autoxidation and Autoxidants*, Vol. I, W. O. Lundberg, Ed., Interscience, New York, 1961, pp. 65–77.

25. P. M. Norling and A. V. Tobolsky, *Thermal Stability of Polymers*, Vol. I, R. T. Conley, Ed., Interscience, New York, 1970, pp. 137–152.

26. C. von Sonntag, M. Dizdaroglu, and D. Schulte-Frohlinde, *Z. Naturforsch.*, Teil B, **31**, 857 (1976).

27. J. A. Church, *Tappi*, **48**, 185 (1965).

28. I. K. Walker, W. J. Harrison, and A. J. Reed, *N.Z. J. Sci.*, **12**, 98 (1969).

29. F. Shafizadeh and Y. Z. Lai, *J. Org. Chem.*, **37**, 278 (1972).

30. F. Shafizadeh and Y. Z. Lai, *Carbohydr. Res.*, **42**, 39 (1975).

31. F. Shafizadeh, *Appl. Polym. Symp.*, **28**, 153 (1975).