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THE COMPARISON OF ACCELERATED AGING CONDITIONS THROUGH THE ANALYSIS OF EXTRACTS OF ARTIFICIALLY AGED PAPER

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This paper presents results from gas chromatographic/-mass spectrometric analyses of extracts of artificially aged paper, and compares the types and quantities of degradation products which result from different sets of aging conditions. The aging of Whatman #1 filter paper at 90°C and 100% RH produces mostly glucose and xylose, which result from hydrolysis of the cellulose and xylan in the wood pulp-derived paper. Dry oven aging at 90°C and above yields product mixtures which contain very little glucose, which indicates that hydrolysis of cellulose is at most a minor reaction under these conditions. Dry oven aging at 150°C produces a mixture of degradation products quite different from those formed at lower temperatures.

Introduction

Accelerated aging is an attempt to simulate in a short time the effects of long periods of natural aging. Its purpose is to evaluate the permanence of materials, or the effects of treatments on the permanence of materials. Accelerated aging can consist of exposure to changes in any combination of potentially damaging environmental factors including heat, humidity, light, oxygen, and pollution. The underlying assumption of accelerated aging is that it simply speeds up the changes (degradation) which occur during normal aging. A material which has been subjected to accelerated aging is assumed to be identical to the same material aged for a longer time under "normal" conditions. Physical, chemical, and/or spectroscopic tests are then used to determine the suitability of materials or the effects of treatments.

More extreme accelerated aging conditions yield results more quickly (and often more obviously), but there are limits to how far accelerated aging conditions can be pushed. In the case of cellulose, the limits within which accelerated aging is equivalent to natural aging have not been well defined, nor is there a widely accepted set of standard aging

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conditions. Because cellulose is such a stable material, it invites (necessitates?) the use of extreme aging conditions. Researchers have used aging conditions which range from very mild to nearly as extreme as conditions known to produce degradation processes very different from those of normal aging. It is therefore difficult to compare the results of the various research papers. The main question to be answered before a set of accelerated aging conditions will be widely accepted is: How extreme can accelerated aging conditions be before they are no longer related to natural aging? The answer to this question depends on an adequate comparison of the effects of aging conditions. How can two sets of aging conditions be compared?

The Kinetics of Degradation

The degradation of cellulose occurs through a number of reactions and is affected by a number of external factors. For degradation under two sets of aging conditions to be considered comparable, the following requirements must be met: 1) the same reactions must take place under both sets of conditions; 2) the relative rates of the various reactions should be similar during both sets of conditions. In other words, accelerated aging should speed up all reactions by the same factor without introducing new reactions. This is easy to state, but not to test experimentally. One problem is that most of the tests which are used to evaluate the degradation of cellulose are not reaction-specific. They involve the measurement of secondary or tertiary properties, such as tear strength, fold endurance, and brightness, which depend on many aspects of the chemistry and physical state of the cellulose. For example, oxidation, hydrolysis, crosslinking, and thermally induced changes in the degree of crystallization can all affect the fold endurance of cellulose. It is possible to use combinations of tests and conditions to follow specific types of reactions, but individual reactions can rarely be followed. A consideration of the kinetics of a simple two-reaction system can demonstrate some of the problems involved in measuring bulk properties.

The rate constant, k, for a reaction is given by the Arrhenius equation

$$k = A \cdot \exp(-E/RT)$$

where A is the Arrhenius factor (a reaction-specific constant), exp is the exponential function, E is the activation energy for the reaction, R is a universal constant, and T is the temperature in degrees Kelvin. The rate for a simple one-step reaction between two components X and Y is the product of the rate constant for that reaction and the activities [X] and [Y] of the reactants (activity is related to and sometimes equal to the concentration). For the reaction of reagents X and Y, the equation is

$$\text{Rate} = [X] \cdot [Y] \cdot k$$

Substituting for k using the Arrhenius equation,

$$\text{Rate} = [X] \cdot [Y] \cdot A \cdot \exp(-E/RT)$$

For constant conditions during the initial stages of degradation, the concentrations of the reactants can be considered constants, and can be combined with A to give another constant A',

$$\begin{aligned}\text{Rate} &= A' \cdot \exp(-E/RT) \\ &= k'\end{aligned}$$

This is equivalent to the equation for the rate constant k, except that it now depends on the reactant concentrations which were combined with A to give A'. This k' is the type of "k" usually determined in cellulose degradation experiments, where the nature and roles of the various reactants often are not clear. It is not feasible to factor out reactant concentrations in this case. A' and k' can be mathematically manipulated in the same ways that A and k can be, but one must remember that A' and k' depend on reactant concentrations, which in turn can be affected by the aging conditions. For instance, changing the relative humidity can change A' and k' if water is one of the reactants.

The rate constant k' can be determined for a specific set of conditions by monitoring the progress of the reaction over a period of time. If k' is determined for more than one temperature, then A' and E can be determined by taking the natural log of both sides of the rate equation

$$k' = A' \cdot \exp(-E/RT)$$

to give

$$\ln(k') = \ln(A') - E/RT$$

A plot of ln(k') versus 1/RT (the "Arrhenius plot") is a straight line of slope -E which intercepts the y axis at ln(A'). These equations apply if a single reaction is involved. If, instead of measuring the rate of a single reaction, one monitors the rate of change of a property which is affected by more than one degradation reaction, then the plot thickens (no pun intended).

If the property being measured changes linearly with the progress of each of two degradation reactions, then the rate of change of the property is proportional to the sum of the rates of the two reactions:

$$\begin{aligned}k_{total} &= k_1' + k_2' \\ &= A_1' \cdot \exp(-E_1/RT) + A_2' \cdot \exp(-E_2/RT)\end{aligned}$$

The apparent activation energies for changes in many of the properties of paper have been determined. The activation energies for some important cellulose degradation processes which involve only one

type of reaction are very similar, and some differ by less than the amount of experimental error.[1] This has interesting consequences, for if E_1 and E_2 have the same value E, then the last equation becomes

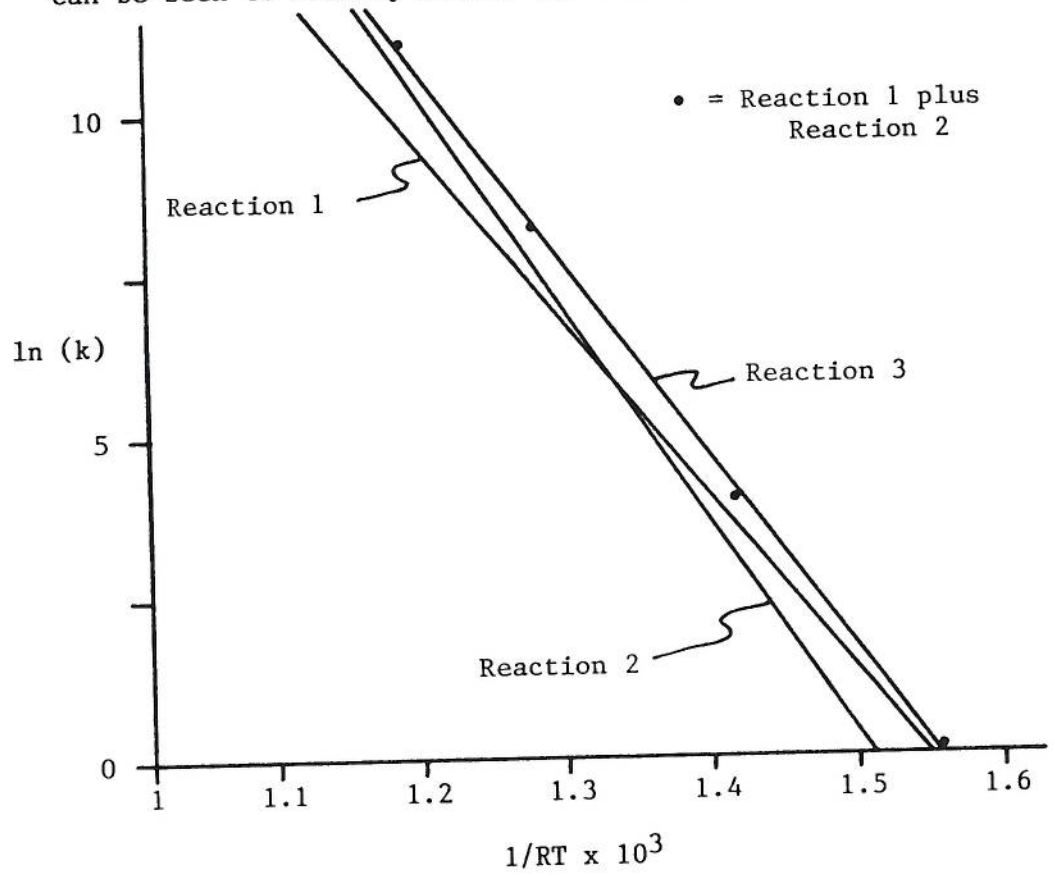
$$k_{total} = A_1' \cdot \exp(-E/RT) + A_2' \cdot \exp(-E/RT)$$
$$= (A_1' + A_2') \cdot \exp(-E/RT)$$

Determining the reaction rate at different temperatures allows one to determine E and the sum $(A_1' + A_2')$, but does not allow one to determine A_1' or A_2'. This means that it is not possible to calculate the relative contribution of the two reactions. It is not even possible to determine if one of the reactions does not occur at all under the specific conditions used! Since A_1' and A_2' are functions of the aging conditions, changing the conditions may alter the rates of one or both reactions. This cannot be detected if one looks only at the activation energy, because the plot of $\ln(k_{total})$ versus 1/RT is still a straight line with a slope of -E. The plot is shifted, however, so that while it is parallel to the plot for the old conditions, its y axis intercept is the new value of $\ln(A_1' + A_2')$. For example, an analysis of experimental data showing a parallel shift of Arrhenius plots with a change in humidity has been reported.[2]

The argument above can be extended to any number of reactions with similar activation energies. Even if the activation energies are not equal, it is still difficult to use tests which are not reaction-specific to sort out the various reactions. Plots of $\ln(k_{total})$ versus 1/RT are still often linear within experimental error. The "activation energy" determined from the plot will be an average of the activation energies of the reactions. This can be demonstrated by looking at data calculated for hypothetical reactions with typical activation energies. Figure 1 shows a plot of ln(k) versus 1/RT for two reactions between 50 and 150°C. Reaction 1 has an activation energy E_1 of 27 kcal/mol, Reaction 2 an E_2 of 33 kcal/mol. A_1 and A_2 have been adjusted so that the rates of the two reactions are the same at 100°C. The log of the sum of the two reaction rates, which one would determine by measuring a property affected by both reactions, is plotted at four points. The data points for the sum of the two reactions are nearly co-linear, and closely follow the plot for a third individual reaction, Reaction 3, which has an activation energy E_3 of 29.78 kcal/mol. Data such as the plotted points are not sufficient to determine whether one or two (or more) reactions are occurring, much less to determine the relative rates of individual reactions. Simple reaction systems yield straight-line Arrhenius plots, but straight-line Arrhenius plots do not imply a simple system.

The above discussion required a number of simplifying assumptions. The actual aging process of cellulose is more complex. Degradation products may themselves undergo reaction. Portions of the cellulose (such as the non-crystalline regions) may react completely so that reactions involving them stop, causing data plots that are initially linear to curve or change slope as aging continues. Most of these

Figure 1. A plot of ln (k) versus 1/RT for three hypothetical reactions with activation energies E_1 = 27, E_2 = 33 and E_3 = 29.78 kcal/mole, and Arrhenius constants of A_1 = 1.54E+18, A_2 = 5.00E+21 and A_3 = 1.40E+21. Points for ln (k_1+k_2) are also plotted and can be seen to closely follow the line for Reaction 3.



The calculated values used for the plots in Figure 1.

Temperature °C	1/RTx10^3 T in °K	ln k_1	ln k_2	ln k_3	ln(k_1+k_2)
50.0	1.56	-0.13	-1.38	0.06	0.13
60.0	1.51	1.14	0.17	1.45	1.46
70.0	1.47	2.32	1.62	2.76	2.72
80.0	1.42	3.44	2.99	3.99	3.93
90.0	1.38	4.50	4.28	5.16	5.09
100.0	1.35	5.51	5.51	6.27	6.20
110.0	1.31	6.46	6.67	7.32	7.26
120.0	1.28	7.36	7.77	8.31	8.28
130.0	1.25	8.21	8.82	9.25	9.25
140.0	1.22	9.03	9.81	10.15	10.19
150.0	1.19	9.81	10.76	11.01	11.09

problems and complexities can be avoided by monitoring individual reactions rather than properties dependent on more than one reaction. Aging conditions can then be compared directly; there is no need to manipulate the data or to make assumptions as to which kinetic model is appropriate.

Determining the concentrations or relative quantities of degradation products is one means of following the individual reactions that produce them. If changing the aging conditions (from "natural" to "accelerated", for example) causes changes in the types or proportions of degradation products, then the reactions producing the products must not have occurred to the same extent. The aging conditions are not comparable. If changing the aging conditions causes little change in the degradation product mixture, then the net aging process which produces the products has not been affected. A series of experiments with different sets of aging conditions will determine the degree to which aging conditions can be changed without affecting the aging process. We have used the concentrations of a number of degradation products of cellulose to determine the effects of changes in temperature and humidity on the aging process.

Experimental Aging Conditions

Samples of Whatman #1 filter paper were aged for four different lengths of time for each of four different aging conditions. Shorter aging times were used at higher temperatures. Aging was conducted at 90°C at both low (dry oven) and high (100% RH) humidity, and at 120 and 150°C in a dry oven. These conditions were chosen for several reasons. They are simple conditions to achieve, and are similar to conditions which many researchers use. They include the most extreme conditions likely to be encountered in the literature, and also the largest possible span of relative humidity. These conditions, if any, should exhibit differences in aging effects. If differences between low and high humidity are seen at 90°C, an anticipated argument is that the lower humidity requires higher temperatures for reactions involving water to take place. Thus, dry aging at higher temperatures (120 and 150°C) is included. And lastly, conducting the initial experiments using the most extreme conditions yields results quickly. These results should help to improve the design of more time-consuming experiments using milder conditions.

Analysis of Degradation Products

The potential degradation products of a highly purified, delignified wood pulp paper include sugars (especially glucose) and their oxidation, dehydration, and fragmentation products. The analyses conducted for this work were designed to detect sugars and sugar-like compounds of 4 to 6 carbons. This includes glucose, a 6-carbon sugar which is the building block for cellulose, and other monosaccharides such as xylose, which is a 5-carbon sugar found in wood. Degradation products of these sugars, such as oxidation and dehydration products, should also be

detectible. Higher molecular weight degradation products, such as cellulose fragments containing more than one glucose unit linked together, were not considered.

The procedure consists of the following: The aged paper samples are extracted with water, and the solutions are evaporated. Sugars in the residue with carbonyl groups are converted to oximes, and then all hydroxyl groups are trimethylsilylated. The resulting TMS-oximes are volatile enough to be separated and analyzed by gas chromatography/mass spectrometry. The mass spectra acquired for each component of the mixture should help in the identification of at least the class of compound (aldose, ketose, anhydro- sugar) and give some idea of the type of reaction which produced it. Relative and/or absolute quantities of the components can be calculated. Peak areas, retention times, and mass spectra of the degradation products resulting from one set of aging conditions can be compared with those of another set of aging conditions to determine if the same products are produced in the same quantities.

Results

Figure 2 shows the chromatograms obtained for the samples aged at 90°C at 100% RH and at 90 and 150°C in a dry oven. The chromatograms for the 120°C dry oven samples are similar to those for the 90°C dry oven samples and are not included. The scale for each chromatogram is different and was chosen so that the largest peak is full height. Quantitative data and some identifications are presented in the Table. A zero quantity does not necessarily mean that no peak was present; in some cases the peaks were too small or not high enough above background to be accurately quantified.

Glucose and xylose were definitely identified, their peaks are labelled in the chromatograms. The derivatization method results in two adjacent peaks for each of these compounds. This was verified by running reference samples. The areas of the appropriate peaks were combined to give the glucose and xylose values in the Table. Some other peaks are identified by class of compound in the Table. Mass spectrometry was not sufficient to differentiate between the many possible stereoisomers. Exact identification of the specific sugars would require running reference samples of all the possible compounds.

The recorded quantities are not highly accurate; the values for weak peaks especially may err by a factor of two. Because the chromatographic peaks were extremely sharp (some are only a second or so wide), and mass scanning took one second, not enough mass spectra were collected per peak to reconstruct the peak shape accurately. Analog detectors with response times faster than one second should produce better quantitative data. These will be used in later experiments when mass spectral data are no longer required for the identification of degradation products. Despite this problem, the data are consistent in allowing components to be considered as major, minor, or trace degradation products.

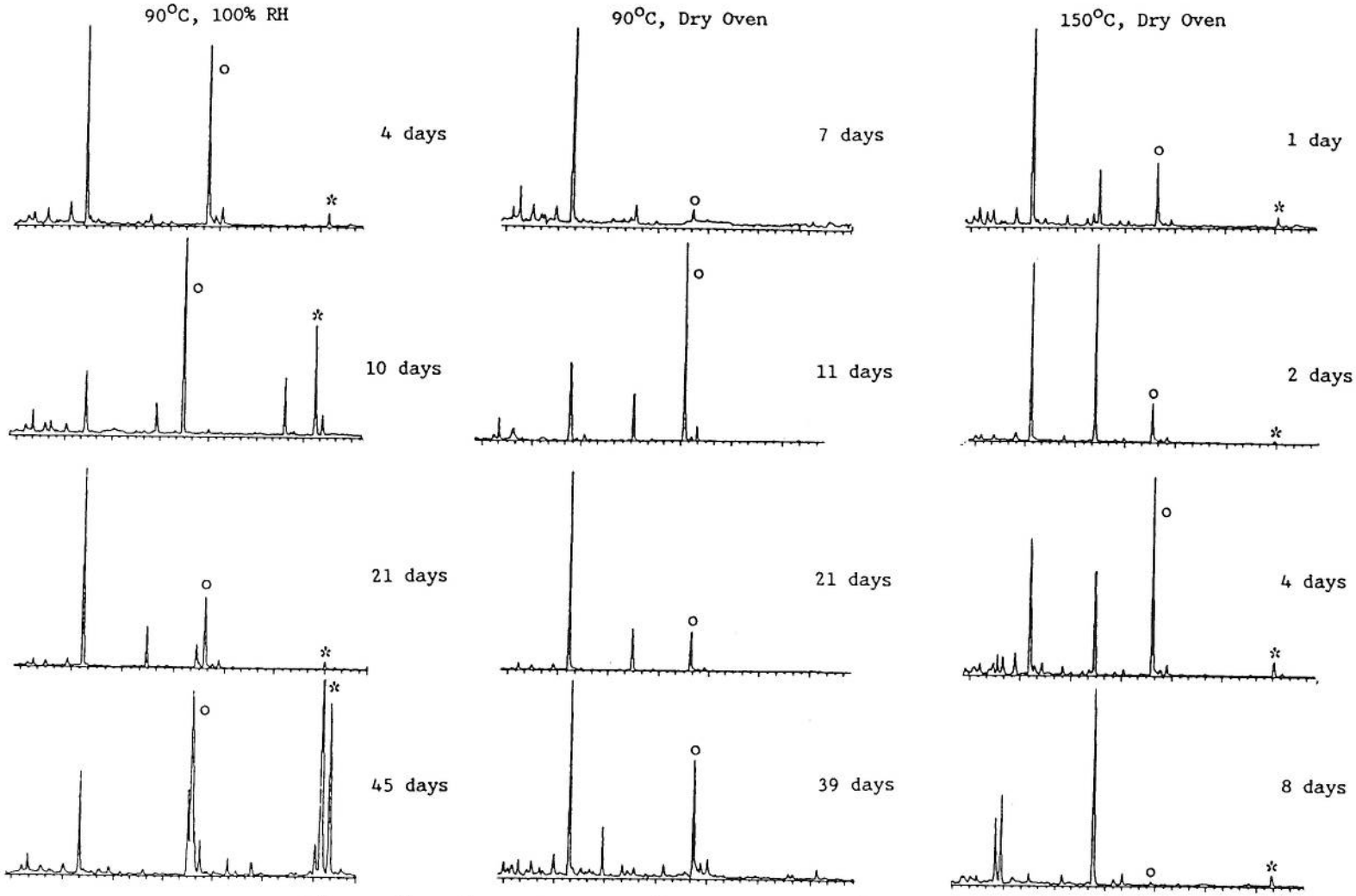


Figure 2. Chromatograms for extracts of aged paper.
Labelled peaks: * = glucose, o = xylose.

TABLE. Quantities of Extractible Degradation Products in Artificially Aged Paper in Mg/100 G paper.

	90°C, 100% RH Days Aged				90°C, Dry Oven Days Aged				120°C, Dry Oven Days Aged				150°C, Dry Oven Days Aged			
	4	10	21	45	7	11	21	39	1	2	4	18	1	2	4	8
1.	0.5	0.0	2.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.0
2.	2.2	1.5	6.0	5.2	1.1	2.6	0.8	1.9	0.8	1.7	1.2	1.3	1.7	1.8	4.1	4.7
3.	2.2	2.5	3.0	12.4	2.4	4.2	1.6	1.0	2.3	3.4	4.0	1.2	1.6	1.7	1.8	2.8
4.	0.0	0.0	0.0	0.0	0.3	0.0	0.0	1.2	0.2	0.3	0.3	0.0	2.4	0.0	0.0	0.0
5.	3.3	2.3	6.2	7.5	2.3	5.8	1.9	3.0	1.7	4.4	1.8	1.4	2.8	2.1	4.8	1.8
6.a pentose ?	0.9	2.2	2.4	1.6	1.2	0.0	0.6	1.4	1.4	0.0	0.0	0.0	0.0	0.0	5.4	19.9
7.a pentose ?	1.4	0.0	2.2	0.0	1.5	1.1	0.6	1.0	1.2	0.1	0.5	0.9	0.7	0.0	8.1	25.8
8.	5.2	1.7	7.6	10.9	1.2	3.1	1.9	3.0	0.3	4.0	3.6	1.8	2.7	2.5	8.9	4.6
9.an aldopentose ?	32.9	11.9	82.3	56.7	21.0	18.9	22.3	25.0	4.1	31.9	20.1	12.8	31.5	17.3	53.6	4.1
10.	0.0	0.0	1.9	4.3	0.0	0.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.6	0.0
11.	1.5	0.0	3.3	2.3	1.1	1.8	0.8	1.8	0.0	1.9	0.8	1.1	1.0	0.9	4.8	0.6
12.	0.0	1.1	2.3	6.7	1.1	1.1	0.0	1.8	0.4	0.9	0.0	0.0	0.8	1.3	0.0	0.8
13.	0.0	0.0	0.2	7.5	0.0	0.0	0.0	4.8	0.2	0.0	0.7	0.8	1.4	1.3	2.0	3.2
14.	0.3	0.6	2.5	2.1	0.7	0.6	0.1	0.3	0.2	0.3	0.0	0.0	1.1	0.0	0.0	2.3
15.	0.8	0.0	3.1	0.0	0.5	0.0	0.6	1.5	0.4	0.8	0.4	0.0	1.0	0.8	0.7	0.8
16.	1.0	0.7	2.5	0.0	0.8	0.7	0.4	1.0	0.3	1.0	0.0	0.5	2.3	1.1	2.6	1.5
17.a pentose	2.8	4.8	15.1	3.2	2.1	10.0	6.0	1.1	5.1	26.5	9.7	10.2	7.5	17.7	41.5	68.4
18.	0.7	0.0	3.2	1.5	0.6	0.0	0.1	0.4	0.2	0.3	0.0	0.5	0.5	0.7	0.6	0.4
19.	1.0	0.0	3.5	0.0	0.4	0.8	0.5	0.0	0.3	1.8	0.0	0.5	0.7	1.1	1.0	2.2
20.	0.4	0.0	0.8	0.6	0.0	0.0	0.4	1.6	0.0	0.0	0.3	0.7	0.8	1.0	1.8	3.3
21.xylose	32.1	28.6	53.9	290.2	2.6	28.1	7.0	23.5	0.0	13.2	0.0	2.7	10.5	6.3	55.3	1.1
22.	2.3	0.0	3.9	4.7	0.0	1.2	0.7	3.5	0.0	0.7	0.0	0.0	0.3	1.1	2.7	0.0
23.	3.4	0.0	4.7	3.6	1.5	2.3	1.2	3.5	0.1	1.3	0.0	0.7	1.0	1.8	3.6	0.0
24.an aldopentose	0.2	0.0	2.8	11.1	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.6
25.a 4-keto aldohexose	0.0	0.0	0.0	3.0	0.0	0.0	0.0	0.0	0.1	0.1	0.0	0.0	0.1	0.0	0.0	0.0
26.a 4-keto aldohexose	0.3	0.0	0.0	0.9	0.0	0.0	0.0	0.0	0.1	0.2	0.0	0.4	0.4	0.0	0.2	0.2
27.an aldopentose ?	0.5	0.0	2.3	11.2	0.0	0.4	0.0	0.0	0.3	0.4	0.0	0.1	0.3	0.0	0.0	1.3
28.an aldopentose	0.0	0.0	0.0	2.7	0.0	0.0	0.0	0.0	0.1	0.4	0.0	0.0	0.0	0.0	0.0	0.0
29.an aldohexose	0.3	0.5	1.2	4.1	0.0	0.2	0.0	0.7	0.5	0.7	0.0	0.3	0.2	0.5	0.4	0.7
30.an aldohexose	0.3	0.7	1.4	2.3	0.0	0.2	0.0	0.7	0.4	0.6	0.0	0.4	0.3	0.0	1.0	1.5
31.	0.3	0.0	6.8	7.5	0.0	0.0	0.3	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0	1.1
32.an aldohexose	0.0	0.0	0.0	27.8	0.0	0.0	0.5	0.0	0.0	0.0	0.0	0.0	0.0	1.0	0.0	0.0
33.glucose	2.7	17.6	8.8	346.4	1.8	0.5	0.0	2.0	0.6	0.7	0.8	2.2	1.7	0.0	7.2	5.6
34.a dialdohexose ?	0.0	0.0	0.0	6.3	2.1	0.0	0.0	0.0	0.0	0.9	0.0	0.4	0.0	0.0	0.8	0.0
35.a dialdohexose ?	1.0	0.0	0.0	12.7	0.0	0.0	0.0	0.0	0.0	0.7	0.0	0.0	1.0	0.0	0.4	0.9
36.a dialdohexose ?	0.0	0.0	0.0	5.0	0.0	0.0	0.0	0.0	0.3	0.0	0.0	0.7	0.3	0.0	0.3	0.0
37.a dialdohexose ?	0.0	0.0	0.0	2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.6	0.0	0.0	0.0	0.0
Total	100.3	76.7	236.6	863.7	46.1	84.5	48.2	85.6	21.7	99.8	44.2	42.2	76.2	62.1	218.0	166.1

An analysis of an extract of fresh paper showed that some of the same compounds, including glucose, are present, but only in unquantifiable trace amounts. Therefore, the compounds seen in the analyses of aged paper are products of aging, and are not present as extractible material in the original paper.

Discussion

Glucose is produced quickly during humid aging. After 45 days it is the major product, at 346 mg/100 g paper accounting for 40% of the total extractibles. One explanation for the huge increase in glucose in the last half of the humid aging period (between 21 and 45 days) is as follows: Initially, most of the cellulose chains are quite long, and hydrolysis at the end glucose unit (which frees a molecule of glucose) is less likely than hydrolysis somewhere in the middle of the cellulose molecule. Hydrolysis at this stage does not produce many single glucose molecules. When a hydrolysis reaction breaks a cellulose chain, it produces two shorter chains with two more glucose end units. As hydrolysis proceeds, the number of glucose end units increases geometrically. Thus, the number of single glucose molecules hydrolyzed from the ends of the shorter cellulose chains increases dramatically, even if the rate of hydrolysis remains constant. No such dramatic increase was seen in any of the dry aging experiments; the glucose concentration is always less than 8 mg/100 g of paper, and never exceeds 5% of the total product. This indicates that hydrolysis of cellulose occurs at a much slower rate during dry aging, if at all (mechanisms other than hydrolysis might account for the relatively small amounts of glucose produced). It is also possible that the glucose which is produced during dry aging is from more readily accessible regions of the cellulose structure, such as the non-linear hemicellulose portion or the non-crystalline regions of the cellulose. These areas may produce the limited amount of glucose seen in dry aging. Hydrolysis of the crystalline cellulose regions may not occur at very low humidities because there is not enough water to cause swelling and make the cellulose molecules more accessible to reaction. Even after 8 days at 150°C in a dry oven, when the paper is all but caramelized, no more than small amounts of glucose are produced.

A similar but less pronounced situation occurs with xylose. Xylose is a wood sugar usually present in the form of xylan, a polymeric form of xylose. Xylose has been reported as a component of polysaccharides extracted from Whatman #1 filter paper.[3] As with glucose, hydrolysis is required to free the xylose. As with glucose, humid aging produces much xylose quickly, and the amount increases dramatically during the last half of the aging period. Dry aging produces more xylose than glucose, but still less xylose than is produced during humid aging. Xylan is less resistant to hydrolysis than cellulose, even at low humidities when it is not swollen with water.

Other differences exist. Peaks 24-37 (including glucose) are all present in the later stages of humid aging, but are not significant

during dry aging. Mass spectral data show that most of these compounds are stereoisomers of glucose or their oxidation products. They may result from the stereochemical rearrangement (racemization) or oxidation of glucose. Racemization is a process which, like hydrolysis, should proceed faster at higher humidities. Cellulose degrades to glucose to a greater extent during humid aging than during dry aging, and glucose itself also seems more susceptible to further reaction during humid aging.

Differences exist even among the dry aging conditions. Peaks 6, 7, and to a lesser extent, 17, are produced in much greater quantity at 150°C (constituting more than two-thirds of the total extract after 8 days) than at either of the lower temperatures, including humid aging at 90°C. These products are an indication that some reactions which occur to only a minimal extent at lower temperatures can become quite important at higher temperatures.

An anomaly exists in the 150°C data. Peaks 9 (a pentose) and 21 (xylose) are present in the first three samples, but the amounts drop off substantially in the last sample. This may be due to further reaction of these compounds, such as rearrangement to compounds seen as other peaks, or to reattachment of these compounds to the cellulose structure by reactions which produce crosslinks.

There seem to be no significant differences between 90 and 120°C dry oven aging.

Conclusions

We have developed a method for the analysis of a number of the extractible degradation products of cellulose. We have used this method to compare directly the aging processes for different aging conditions, and to show that different aging conditions can produce quite different mixtures of degradation products in cellulose. The major reaction of humid aging at 90°C is hydrolysis. Dry-aged samples show no indication of more than a minor degree of hydrolysis, and the hydrolysis which does occur is probably limited to more accessible regions of the cellulose structure. Temperature also has an effect; the major reactions taking place at 150°C hardly occur at lower temperatures. Experimental work at lower temperatures and at moderate humidities is required to establish the relationship of these results to those of natural aging.

Experimental Details

Sheets of Whatman #1 filter paper, a highly cellulosic delignified wood-pulp paper, were used in the experiments. Dry aging was conducted at constant temperature in a dry oven vented by room air at 22°C, 50% RH. For 100% RH aging, paper samples were placed in a polypropylene beaker which floated in liquid water in a closed polypropylene container. Teflon tape was used to make the seal tight. The loss of water during the course of the experiment was minimal. There was no

condensation of liquid water in the beaker containing the paper samples. No special effort was made to exclude oxygen, but the access of oxygen was probably limited after the container was sealed.

The paper samples were cut into small pieces and extracted with 100 ml of deionized water/635 mm^2 (5.5 g) of sample. The mixture was stirred for 2 hours with a Teflon-coated magnetic stirrer, and then filtered through (what else?) Whatman #1 filter paper. Several 5 ml aliquots of the filtrate were placed in pre-weighed reaction vials, and dried in a vacuum desiccator.

The weights of the residues of the 5 ml aliquots ranged from 0.1 to 2.7 mg. The total extract was thus about 0.04-1% of the original weight of the paper. The residue weights were not determined very accurately since the tare weights (of the thick-walled reaction vials) were so large. The residue weights were measured only to determine the amounts of derivatizing reagents to be used. For residue weights of more than 1.5 mg, 0.2 ml of each reagent was used; 0.1 ml was used for smaller residue samples.

The first step of derivatization consists of adding 0.1 or 0.2 ml of STOX[4] to each sample, sealing the vial, heating at 72°C for 1.5 hours, and allowing it to cool. STOX is a reagent mixture containing 25 mg/ml hydroxylamine hydrochloride and 6 mg/ml of O-phenyl β-D-glucopyranoside (an internal standard) in pyridine. This step converts any carbonyl groups of components in the residue to oximes.

The second step consists of adding 0.1 or 0.2 ml (the same quantity as of STOX) of trimethylsilylimidazole in order to trimethylsilylate all hydroxyl groups (including the oxime hydroxyl groups). The vial is again sealed, allowed to stand for at least 30 minutes, and analyzed on a gas chromatograph/mass spectrometer (Carlo Erba model 5300/-Finnigan-MAT model 8230).

The gas chromatographic conditions are: DB-1 (bonded polydimethyl-siloxane) fused silica capillary column, 30 m x 0.32 mm i.d., split ratio approximately 100:1. The starting temperature is 100°C, which is immediately raised by 10°C/min to 275°C. Injection volumes are 1 microliter.

No GC/MS interface is used; the column feeds directly into the source of the mass spectrometer. Electron impact spectra are collected at a scanning speed of 1 sec/decade. Magnetic mass scanning is from 70-700 mass units at a resolution of 1000. A background is determined and subtracted from each mass spectrum.

The per-trimethylsilylated O-phenyl β-D-glucopyranoside served as an internal calibrant for both retention time and concentration. Each sample was run at least twice. Samples were stable for a working day, but had degenerated badly after 24 hours. A blank consisting of only the derivatizing reagents was also analyzed. It contained some small

peaks which eluted at the beginning and end of the chromatographic run. The chromatograms in Figure 2 are the span between these peaks; this portion of the chromatogram includes all of the observed sample peaks. To see if extractible sugars are present in the fresh paper, a reference sample of an extract of unaged Whatman #1 filter paper was analyzed. Only minute traces of sugars (including glucose) were found, and then only by looking for characteristic peaks in the mass spectra. No corrections to the sample data were required for the small amounts found.

Notes and References

1. Roberson, in a search of the literature, found activation energies in the general range of 26 to 29 kcal/mol for the hydrolysis of cellulose, and an activation energy of 20-30 kcal/mole for the crosslinking of cellulose (David D. Roberson, "The evaluation of paper permanence and durability," Tappi 59(1976):63-69). Springer reported an activation energy of 28.2 kcal/mol for the removal of xylan (a polymer of the wood sugar xylose) from wood by acid hydrolysis (Edward L. Springer, "Hydrolysis of Aspenwood Xylan with Aqueous Solutions of Hydrochloric Acid," Tappi 49(1966):102-106).

2. Ira Block, "Temperature and Humidity Effects in the Accelerated Aging of Cellulosic Textiles," in ICOM Committee for Conservation, 7th Triennial Meeting, Copenhagen, 10-14 September 1984, Preprints, Working Group: Textiles, vol. I, pp. 84.9.7-84.9.10.

3. G. W. Huffman, et al., "Nature of a Hemicellulose Extracted from Cellulose with Water," Nature 175(1955):990-991.

4. STOX is the trade name of a product available from Pierce Chemical Company, P.O. Box 117, Rockford, IL 61105.