

## Determination of the Cellulose Scission Route in the Hydrolytic and Oxidative Degradation of Paper

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### INTRODUCTION

Since the service life of paper is generally thought to depend on the rate of the chemistries that cleave the cellulose polymer, the knowledge of the dominant cellulose scission reaction is of central importance to the design of effective preservation strategies. Treatment strategies must be targeted to retard specific scission chemistries, and in order to validate the effectiveness of these treatments, artificial aging tests must be used to accelerate the same degradation chemistries which dominate the natural aging. For papers containing high levels of acids or oxidation catalysts, or for papers subjected to oxidizing bleaches or pollutant gases, reasonable inferences can often be made of the dominant degradation chemistry causing strength loss. Most papers, however, are not subjected to these extremes, and hydrolytic and oxidative scission may both seem possible degradation paths. As a result, there often remains considerable uncertainty about which degradation route dominates the strength loss for a particular aging paper.

We would like to establish the nature of the scission chemistry, so we can predict the effect of conservation treatments and preservation measures. Knowledge of whether strength is lost predominantly by hydrolysis, which is acid-catalyzed, or by direct oxidative cleavage, which may occur more rapidly at neutral or alkaline pH, would allow better prediction of the consequences of pH adjustments. If carbonyl or carboxyl groups are formed, we would like to know whether these occur along the cellulose chains or at the ends, for oxidized groups along the chain might be sites for subsequent "weak link" scissions.<sup>1</sup> The quantity of these interior functional groups might then be an indication of the capacity for future alkaline instability or exacerbated hydrolytic cleavage.

Vulnerable sites along the chain may call for special precautions or stabilizing treatments such as salt applications following an oxidative treatment.

Despite the importance of this knowledge, there is very little direct evidence of the degradation chemistry in an aging paper. The most informative studies have either been those that monitor some intermediate in a reaction, such as the electron spin resonance spectra of radicals produced during photolysis or radiolysis of cellulose<sup>2</sup> or those that characterize the small soluble or volatile products evolved during some degradative treatment.<sup>3</sup> Most of the studies of cellulose degradation involve less direct and quantitative measures of the chemical changes, using pH, copper number or alkali solubility, for example, or rate changes in varied aging environments (such as high or low water or oxygen concentrations) to provide circumstantial evidence of the degradation mechanism.

Although many of these approaches have provided important insight into the mechanisms of cellulose reactions, they have limitations in distinguishing different degradation chemistries during the early stages of paper aging, when some strength remains. Many probes lack specificity to cellulose degradation, for radicals, soluble components, or volatile gases could derive from the reactions of other species in paper besides cellulose. Some analyses lack sensitivity, being able to detect changes only after substantial concentrations of reaction intermediates or products have been formed, so investigations of the early stages of paper deterioration are impossible. Finally, analyses that are not quantitative are of limited value, even though many of these quantities have been found to be related to the degradation.<sup>4,5</sup> The shortcomings of these approaches illustrate two fundamental problems in the quantitative characterization of cellulose that must be overcome if the degradation route is to be established: the extent of degradation, measured by the number of chain scissions, must be accurately determined from molecular weight measurements in the degrading cellulose polymer; and the functional group changes that accompany this degradation must be assayed specifically, sensitively, and quantitatively.

Most functional group analyses developed to analyze cellulose chemistry have proven incapable of this quantitative, selective assay for mildly degraded cellulose. As with all polymers of relatively high molecular weight, drastic molecular weight reductions (and consequent strength loss) of cellulose can occur with only very minor extents of reaction. For cellulose in cotton fibers, for example, scission of fewer than 1% of the total chain links can cause the loss of fiber strength.<sup>6</sup> The very low concentrations of new chain ends in slightly degraded papers which still retain some strength, then, presents a formidable challenge to the analyst who seeks to probe the details of their production.

Another obstacle to assaying functional groups in cellulose is the nature of the carbohydrate itself. In cellulose, one end of the chain consists of a glucose unit having a free hemiacetal form. This terminal structure easily converts to an aldehyde form of the sugar, the chemical reducing power of which leads to their designation as the “reducing” chain ends. Because cellulose chains usually occur with these carbonyl-containing end groups, it is difficult to distinguish the new end groups produced in scission reactions from the carbonyl-containing products of oxidative chemistries or the reactions of low-molecular-weight saccharidic components of paper, such as hemicelluloses. Furthermore, the assay for aldehydes must be able to detect these groups in both the free and acetal forms, and the tendency for carbohydrates to easily form derivatives also complicates the analysis of ketone and carboxyl groups, which can form ketals and lactones, respectively.

A further complexity in probing cellulose scission chemistries arises from the semi-crystalline morphology of the cellulose polymer in paper. The cellulose in a manufactured paper sheet occurs in highly ordered domains called crystallites connected by amorphous domains in which the chains lack a regular arrangement. It is the mobility of the chains in the amorphous regions that lends paper its flexibility, and the anchoring of the chains in the crystallites contributes to the strength and elasticity of the sheet. In general, degradation chemistries tend to occur predominantly in the amorphous regions of this structure, because the crystallites resist the entry of external reagents as well as the disruption of the crystalline order resulting from reaction. Similarly, the impermeability of the crystallites to probe molecules makes analysis of the chemistry within these regions imprecise. For this reason, chemical probes are best targeted to detect reaction in the amorphous regions of the microfibrils, thus avoiding the difficulty of accurately analyzing the mass of largely unreacted and inaccessible cellulose in the crystallites.

To our knowledge, only one study has succeeded in directly probing the cellulose degradation chemistry through the quantitative comparison of chain scissions to functional groups formed on the polymer chain.<sup>7</sup> This study of cotton textile fibers used the hydrazine carbonyl assay<sup>8</sup> and the methylene blue carboxyl assay.<sup>9</sup> These analyses are quite sensitive; they detect only functional groups that reside on insoluble residues, so they target cellulose and neglect soluble materials; and they rely on penetration and reaction of probe dye molecules, so only the permeable amorphous cellulose is examined. Scissions were calculated from changes in molecular weights derived from viscosity measurements, using simple relations to relate viscosity-average and number-average molecular weights.

In this report we present our application of this combination of analyses to

the study of cotton linter filter paper degraded under a variety of conditions. In order to check the validity of this approach, we studied first several degradation reactions that have been reasonably well characterized. These included cellulose exposed to mineral acid, as an example of pure hydrolytic scission chemistry, and cellulose oxidized by periodate, acidic hypochlorite and hydrogen peroxide. The results are then presented for papers exposed to near-ultraviolet and visible light, as well as for papers aged in ovens at several temperatures and humidities.

#### EXPERIMENTAL

For this study, sheets of Whatman No. 42 filter paper were used. This paper is made from cotton linters and has been purified by acid washing to free it of metallic impurities. As a result, the paper is slightly acidic (a cold extraction pH of about 5) due to its carboxylic acid content rather than acid residues from the purification. Sheets of this paper were subjected to various chemical treatments (immersion in 2 N HCl solutions and exposure to vapors above a concentrated HCl solution; 5% unbuffered H<sub>2</sub>O<sub>2</sub>; 3% sodium hypochlorite buffered to pH = 4.5–5 with an acetate buffer; 0.01 M sodium periodate), followed by extensive water rinsing; aged in ovens with either no humidity control ("dry" oven aging at 90°C and 105°C) or with moderate humidity (65% relative humidity (RH) at 80°C, 50% RH at 90°C); or aged under ultraviolet A (UVA) light or simulated sunlight by exposure to the output of fluorescent lamps (Q-Panel UVA-351 and Sylvania F48t12/D/HO, respectively). Light intensities were measured periodically with a radiometer (International Light Model 700). The intensity incident on the samples exposed to the UVA sources was about 2.6 mW/cm<sup>2</sup> between 300 nm and 400 nm, and the daylight fluorescent sources exposed the samples to about 18,000 lx, with a near-ultraviolet intensity of 0.13 mW/cm<sup>2</sup>.

Functional groups and molecular weights were determined after the sheets had been allowed to equilibrate at 23°C, 50% RH for 24 h. Carbonyl contents were assayed using the hydrazine method,<sup>8</sup> and carboxyl contents with the standard methylene blue test.<sup>10</sup> Reported analyses are usually the results of measurements on single samples; values that are averages of two duplicate samples are indicated in the tables. Following an 18-h treatment in unbuffered 0.01 M sodium borohydride to minimize alkaline scission and peeling reactions in the subsequent dissolution, the molecular weight of the cellulose was determined from a measurement of the intrinsic viscosity of a solution of the polymer in cupriethylenediamine hydroxide ("cuene") according to the standard method.<sup>11</sup> The viscosity-average degree of polymerization ( $DP_v$ ) of the unaged

paper was about 1500. Carbonyl and carboxyl contents of the control sheets were about 0.4 mmol/100 g and 0.5 meq/100 g, respectively.

This viscosity-average molecular weight is related to the effective volume of the chains in a given solution, but to calculate the scissions we need the number-average molecular weight ( $DP_n$ ), which is a measure of the average length of chains, rather than their average size. For a simple, most probable molecular weight distribution, the ratio of  $DP_v$  to  $DP_n$  is given by:<sup>12</sup>

$$DP_v/DP_n = [(1 + a)\Gamma(1 + a)]^{1/a}$$

where  $a$  is the Mark-Houwink coefficient for the cellulose/cuene system, and  $\Gamma$  is the gamma function, evaluated by reference to tabulated values.<sup>13</sup> The appropriate value for the Mark-Houwink coefficient is reported to be 0.905,<sup>14</sup> and the above relation yields a ratio of 1.96. The number-average degree of polymerization was thus taken as half the measured viscosity-average degree of polymerization. Since the  $DP_n$  is defined as the total number of monomer units in a sample divided by the total number of molecules, the number of chains is just the total number of monomers (calculated from the sample weight and the molecular weight of a glucose monomer) divided by  $DP_n$ . Expressing the number of chains in the same concentration units as the carbonyl and carboxyl analyses, the concentration of chains in a sample is  $617/DP_n$  mmol/100 g. Since each scission increases the number of chains by one, the increase in this concentration of chains is equivalent to the concentration of scissions that have occurred. Clearly this calculation depends on the validity of the above relations, so we expect this scission determination to become less accurate as the leveling-off degree of polymerization (LODP) is approached, at which point the viscosity becomes insensitive to further decreases in the number-average molecular weight.

The plots that compare the functional groups formed per measured scissions contain data obtained in individual trials. Slopes of the best-fit lines to these data were determined by linear regression. All treatments and exposures were repeated, with the exception of dry oven aging, which required many months to complete. Consequently, the reproducibility of the linear slopes obtained for these long-duration tests cannot yet be assessed.

## RESULTS AND DISCUSSION

### *Acid exposure*

The acid-catalyzed hydrolysis is the most thoroughly studied and understood degradation chemistry of cellulose, and as such it presents the best test of the

success of this analytical approach. Hydrolysis of cellulose should produce one carbonyl per scission, this being the aldehyde group at the new reducing end formed at the chain break. The results of the acid degradation of Whatman No. 42 filter paper are shown in Fig. 1 and Table 1. For both the treatment by dilute acid solutions and by acid vapors, the slope of the best-fit lines to the experimental points indicates the production of  $0.95 \pm 0.01$  carbonyls per scission of the cellulose chain. This result is also in agreement with Dobbelstein's results for acid-treated cotton, where he observed 0.94 aldehyde groups formed per scission.<sup>7</sup> Although many others have demonstrated linear relationships between carbonyl and scission production under similar conditions,<sup>5</sup> to our knowledge this analytical approach is the only one that has quantitatively demonstrated the course of hydrolytic chain cleavage in acid-treated cellulose.

The small discrepancy we observe between the carbonyls expected and measured could be either a reflection of the inherent inaccuracies in the

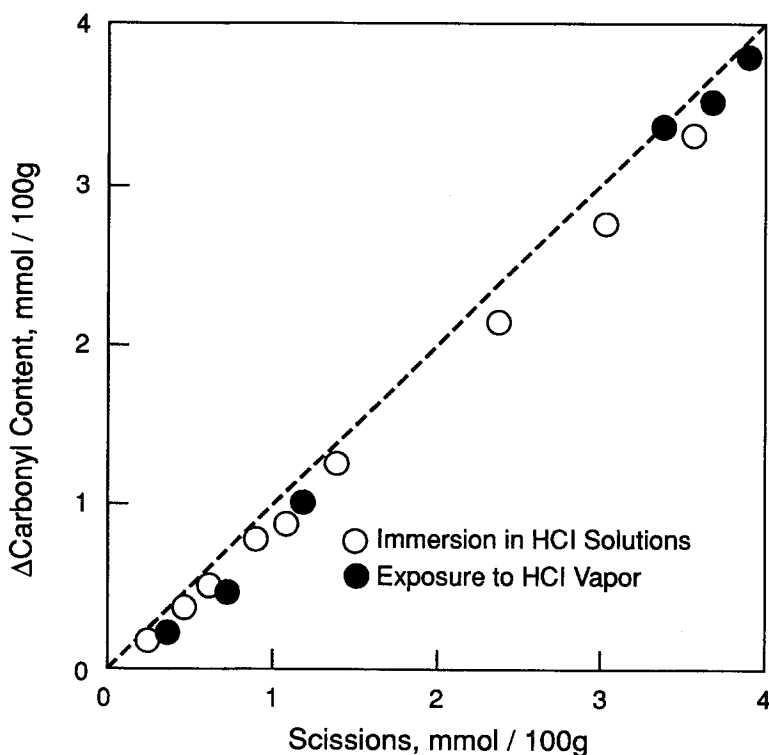


Fig. 1. Carbonyl versus scission production in Whatman No. 42 filter paper exposed to hydrochloric acid solution or vapors. The dashed line represents one carbonyl produced per scission.

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Table 1. Acid hydrolysis of Whatman 42 filter paper

	DP	Scissions (mmol/100 g)	Carbonyl (mmol/100 g)	$\Delta$ Carbonyl (mmol/100 g)
By immersion in 2 N HCl				
control	1478	–	0.36	–
	1166	0.22	0.55	0.19
	987	0.42	0.71	0.35
	855	0.61	0.88	0.52
	715	0.89	1.15	0.79
	643	1.09	1.24	0.88
	553	1.40	1.64	1.28
	378	2.43	2.52	2.16
	314	3.10	3.15	2.79
	277	3.62	3.71	3.35
By exposure to HCl vapor				
control	1459	–	0.40	–
	1046	0.34	0.61	0.21
	789	0.72	0.88	0.48
	600	1.21	1.41	1.01
	287	3.46	3.78	3.38
	268	3.76	3.95	3.55
	255	4.00	4.22	3.82

analyses used or evidence of non-hydrolytic changes. Hydrolysis could be occurring in a region that is not accessible to the hydrazine reagent, thus leading to a slight underestimation of the true number of carbonyls produced, or the scission content may be slightly exaggerated in the estimation of the number-average molecular weight from the viscosity-average molecular weight. Alternatively, the apparent undercounting of carbonyl end groups that must have been formed in the hydrolytic scission may indicate another minor reaction path that slowly consumes carbonyls.

Nevertheless, this functional group assay, which is sensitive and targeted toward degradation in the amorphous cellulose, and the measure of scissions by molecular weight changes, seem well suited to verifying the expected overall hydrolytic reaction in these acid-treated papers. The success of this method in demonstrating hydrolytic product formation gives us some measure of confidence in applying this approach to characterizing paper degrading under other conditions that are less well understood.

*Chemical oxidants*

In contrast to the hydrolytic degradation, reactions of cellulose by chemical oxidants are far from well understood and characterized despite extensive research on specific systems.<sup>15</sup> Oxidation reactions appear to generate products that vary widely, depending on the specific oxidant and reaction conditions such as temperature and pH. Although details of these reactions and products are sketchy because of the lack of precise analysis, certain trends have been established indicating their general course. We have chosen a few of these oxidizing treatments to explore the ability of our analyses to demonstrate the range of oxidation behavior as well as to explore the appearance of oxidation chemistry so that it can be identified when other aging conditions are used.

Fig. 2 and Table 2 show the results of treatments that are known to be predominantly oxidative. Periodate oxidation has been found to be extraordinary in its preferential formation of 2,3 dialdehydes, opening the ring of a glucose unit without cleavage of the cellulose chain itself.<sup>16</sup> Our results reflect this, indicating the creation of significant carbonyl concentrations with almost no accompanying chain breaks, an average of about 25 carbonyls per measured scission.

A more typical oxidant may be the hypochlorite, which has been found to be capable of both oxidative scissions of the chain as well as formation of carbonyls and carboxyls along the unbroken chains. The relative rates of these various reactions have been found to be very sensitive to pH conditions, and at the pH conditions used in this treatment predominantly carbonyl-containing reaction products are reported to be formed.<sup>17</sup> We observed about 4 carbonyls and 0.5–1.5 carboxyls produced per scission. In a similar study of this same oxidant system, Lewin estimated about 8 carbonyls formed per scission in cotton cellulose.<sup>18</sup> It should be noted, however, that the analytical approach used in this earlier work demonstrated about 2 carbonyls produced per scission in hydrolytically degraded cotton.<sup>19</sup> Thus Lewin's data, which suggest that acidic hypochlorite produces about four times the number of carbonyls per scission as hydrolytically degraded cellulose, may be in agreement with our observations.

Since it is likely that, at most, 2–3 of the carbonyls can be located at the chain ends formed during the chain breaking in this oxidant system, the observed product distribution indicates reactions that tend to create both scissions (and end groups) as well as a significant number of oxidized groups at positions along the chains. This outcome is consistent with a picture of the hypochlorite oxidation occurring "randomly", with various sites on the glucose ring being of roughly equal probability for initial attack (in this case, by

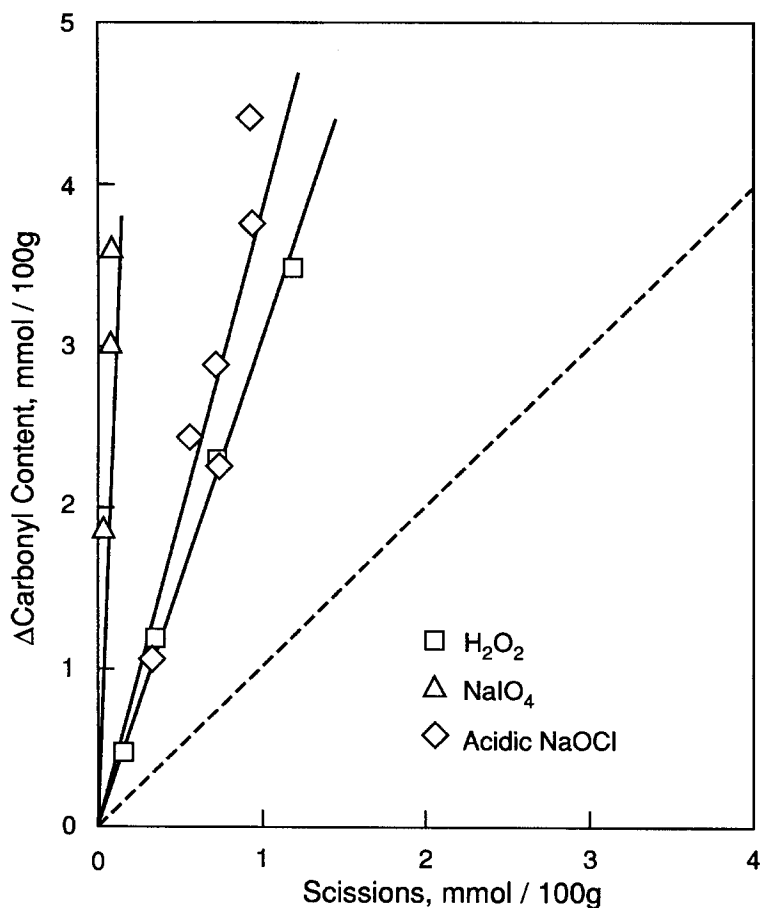


Fig. 2. Carbonyl versus scission production in Whatman No. 42 filter paper exposed to chemical oxidants. The dashed line represents one carbonyl produced per scission.

abstraction of a hydrogen atom by the oxidant). One would expect, then, that oxidative reaction at the 1 and 4 carbons, being on either side of the acetal link in the chain, might lead to scission, whereas attack at the 2, 3 or 6 carbons, being distant from the linkage, might result in carbonyl formation without concomitant chain cleavage.

A similar picture of the cellulose oxidation emerges in the reaction of paper with hydrogen peroxide. Hydrogen peroxide treatment produced about 3 carbonyls and 1 carboxyl per scission. It is impossible with these methods alone to determine how many of the product functional groups reside at chain ends, but it is likely that there are few carbonyls along the remaining cellulose

Table 2. Chemical oxidation of Whatman 42

Exposure (hours)	DP	Scissions (mmol/100 g)	Carbonyl (mmol/100 g)	$\Delta$ Carbonyl (mmol/100 g)	Carboxyl (meq/100 g) <sup>a</sup>	$\Delta$ Carboxyl (meq/100 g)
0.01 M NaIO <sub>4</sub>						
0	1486	—	0.37	—	<sup>a</sup>	
0.5	1505	-0.01	1.37	1.00		
1	1463	0.01	2.23	1.86		
1.5	1402	0.05	3.38	3.01		
2	1349	0.08	3.96	3.59		
3% NaOCl						
0	1459	—	0.41*	-	0.47	—
0.25	684	0.96	4.16	3.75	1.15	0.68
0.50	516	1.55	8.05	7.64	2.25	1.78
0.75	456	1.86	9.48	9.07	3.19	2.72
0	1440	—	0.40*	-	0.48	—
0.10	1018	0.35	1.41*	1.01	0.55	0.07
0.17	866	0.57	2.81*	2.41	0.76	0.28
0.25	770	0.75	2.64*	2.24		
0.33	771	0.74	3.28*	2.88	0.81	0.31
0.50	692	0.93	4.80*	4.40	1.02	0.54
5% H <sub>2</sub> O <sub>2</sub>						
0	1414	—	0.47*	—	0.52	—
1	1191	0.16	0.92	0.45	0.58	0.06
3	980	0.39	1.62	1.15	0.73	0.21
7	761	0.75	2.75	2.28	1.07	0.55
15	587	1.23	3.94	3.47	1.54	1.02
23	444	1.91	6.59	6.12	3.18	2.66
30	382	2.36	7.55	7.08	3.02	2.50

<sup>a</sup> Periodic measurements indicated little or no carboxyl development with this treatment. \* Average of duplicate measurements

chains. Thus in comparison to the reaction with hypochlorite, the oxidative attack under these conditions seems slightly more directed toward pathways leading to scission, and it appears less prone towards producing oxidized groups along the intact chains. It should be noted, however, that both the hypochlorite and peroxide treatments produced a rather wide range of results, and the reported results represent typical, but by no means exclusive, outcomes. This survey of oxidation behavior is clearly too limited to establish any general trends in the reaction of these types of oxidants with paper, and the long history of research on cellulose bleaches underscores the complexity of the oxidation chemistries.

## *The Cellulose Scission Route in the Degradation of Paper*

The systems we have studied nevertheless serve as instructive illustrations of the range of oxidation chemistries that can dominate cellulose degradation and, in particular, the trend for so-called “random” oxidation suggests that such oxidation does not produce an oxycellulose but rather cellulose chains having only a few oxidized sites. There are two implications of this result. First, it suggests that the product of other “random” oxidation chemistries, such as photo-oxidation or atmospheric oxidation, may follow a similar course. Second, the production of relatively few oxidized sites along the chains suggests a limit to the post-oxidative strength loss that might occur through subsequent “weak link” scission at these sites. Depending on how many of the measured carbonyls and carboxyls reside at chain ends (oxidative scissions can produce a variety of end groups containing 0, 1, or more carbonyls or carboxyls<sup>3</sup>), the results observed here indicate that the number of “weak link” scissions cannot exceed 3–4 times the number of scissions produced directly during the oxidation. If significant numbers of these oxidized groups are located at the chain ends, then the post-oxidative scission may be a very small effect. Actual determination of the locations for these products is unlikely, but inferences may be made by measuring the magnitude of the post-oxidative scissions. This is the subject of ongoing work.

### *Light exposure*

Fig. 3 and Table 3 show that exposure to either near-ultraviolet light or simulated filtered daylight created about 2.6 carbonyls per scission and about 0.5 carboxyls per scission (following a minor initial loss of carboxyls). Both the exposures to the UVA source and to the daylight fluorescent source produced the same products per scission, even though the overall degradation was about eight times slower for the exposure to daylight fluorescent lights because of their lower energy dose rate. These results are consistent with the product ratios observed by Dobbelstein, who found 3 aldehydes per scission for cotton exposed to ultraviolet light<sup>7</sup> and by Hon in the early stages of the photodegradation of wood cellulose.<sup>20</sup> The production of more than one carbonyl per scission as well as carboxyl formation are consistent with the view that exposure to light causes predominantly oxidative chemistry to occur.

It may be significant that the product ratios for the light exposure and for “random” oxidants are comparable, for this could indicate that these photo-oxidations are also “random”, perhaps involving similar initial attack by reactive radical species as suggested by others.<sup>21</sup> The photo-oxidation under these conditions seems to be slightly more directed toward oxidative scission than the chemical oxidants studied, with relatively few carbonyls being pro-

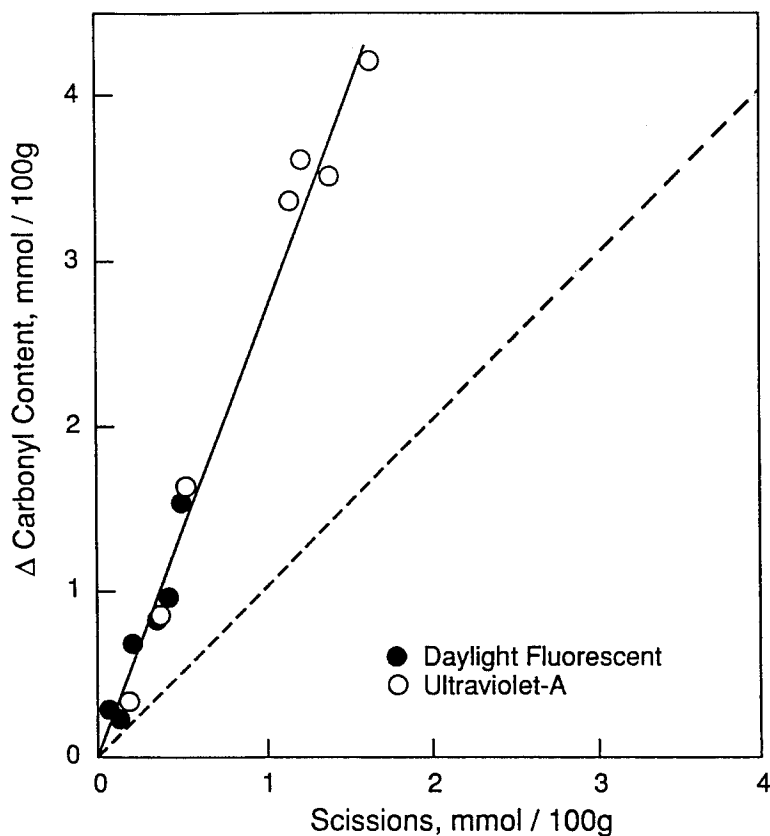


Fig. 3. Carbonyl versus scission production in Whatman No. 42 filter paper exposed to light. The dashed line represents one carbonyl produced per scission.

duced along the chains. This could be the result of a slightly different dominant mechanism than with the "random" oxidants, but it seems more likely that some slight post-oxidative scission may already have occurred during the prolonged exposures. In either case, if a number of these carbonyls were formed at chain ends, and especially if some post-oxidative scissioning had already occurred during the exposures, post-illumination "weak link" scission should be a relatively minor effect. This prediction is in general agreement with previous studies.<sup>22</sup>

#### *Oven aging*

Comparison of aging test results from different laboratories is extremely difficult because each investigator uses quite personal choices for analysis and acceler-

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Table 3. Photochemical aging of Whatman 42 filter paper

Exposure (hours)	DP	Scissions (mmol/100 g)	Carbonyl (mmol/100 g)	$\Delta$ Carbonyl (mmol/100 g)	Carboxyl (meq/100 g)	$\Delta$ Carboxyl (meq/100 g)
UVA radiation						
0	1611	–	0.27	–	0.54	–
24	1322	0.17	0.61	0.34		
74	1085	0.37	1.16	0.89		
168	939	0.55	1.89	1.62	0.58	0.04
468	637	1.17	3.65	3.38		
576	611	1.25	3.90	3.63	0.87	0.33
702	565	1.42	3.80	3.53	0.88	0.34
863	507	1.67	4.49	4.22	1.05	0.51
Daylight fluorescent						
0	1611	–	0.27	–	0.54	
74	1433	0.10	0.50	0.23		
168	1493	0.06	0.56	0.29	0.36	
468	1246	0.22	0.95	0.68	0.41	
702	1102	0.35	1.15	0.88	0.37	
863	1048	0.41	1.25	0.98	0.38	
1372	959	0.52	1.83	1.56	0.42	

ated aging conditions. After decades of study, the oven conditions that will best simulate natural aging for papers have not been, and may never be, uniquely determined. Many different conditions of temperature and humidity have been used to predict aging behavior, and some of these have been suggested as standard tests that, even if they do not simulate natural aging well, at least would provide a basis for interlaboratory comparison. We have studied the degradation produced in Whatman No. 42 filter paper aged in four oven tests to explore the chemical reactions leading to cellulose chain scission in each oven environment. The results are shown in Fig. 4 and in Table 4.

Degradation in the humid ovens produced one carbonyl per scission with no measurable concomitant carboxyl production, which is consistent with a purely hydrolytic scission chemistry. The scission occurred very rapidly at the temperatures used, so that most of the molecular weight is lost after only a few weeks in the humid oven. Aside from the difference in degradation rates, there seems to be no difference in the degradation chemistry occurring at 90°C, 50% RH and at 80°C, 65% RH. Although it is difficult to compare the chain scission rates at these two temperatures because they are not constant during aging, comparing the times to equivalent extents of reaction indicates a degra-

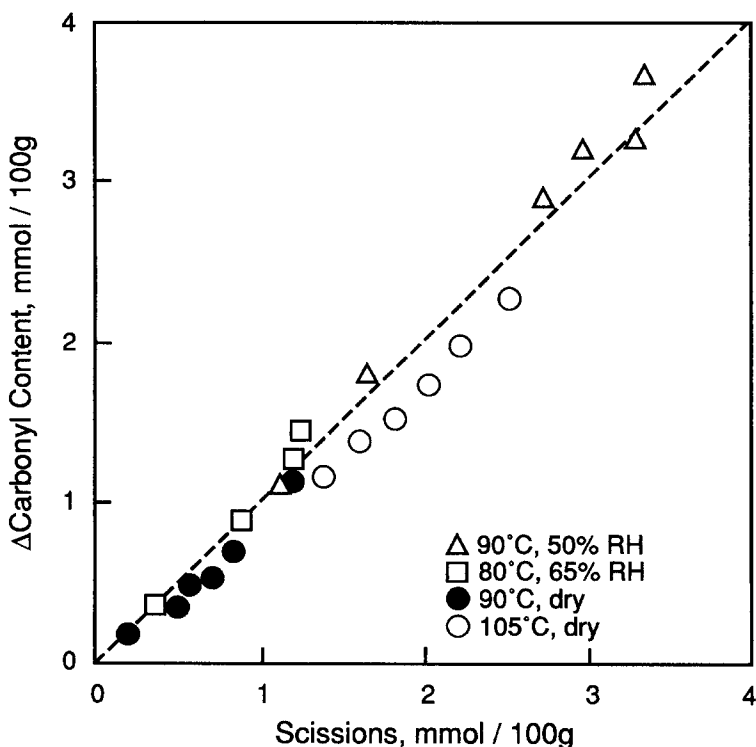


Fig. 4. Carbonyl versus scission production in Whatman No. 42 filter paper aged in various oven conditions. The dashed line represents one carbonyl produced per scission.

ation rate about 2.5 times faster at 90°C than at 80°C. This yields an effective Arrhenius activation energy of about 25 kcal/mol for the pure hydrolytic scission chemistry.

Aging tests were also done in a “dry” oven at 90°C and at 105°C. Although the rate of scission at 90°C in the “dry” oven is about 20 times slower than at the same temperature with 50% RH, the product analysis shows that about one carbonyl is formed for each scission, with no carboxyl group production apparent. At 105°C, dry oven aging also seems to produce about one carbonyl per scission. As with the acid-treated papers, there is apparently a slight undercounting of the carbonyls, probably a result of a slight decrease in accessibility of the fibers from the heat treatment.<sup>23</sup> At this higher temperature, small amounts of carboxyl groups were eventually detected after about 700 h of aging, and the carboxyl content increased slowly thereafter. The scission rate at 105°C was about 4 times greater than at 90°C in the low-humidity

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Table 4. Oven aging of Whatman 42 filter paper

Exposure (hours)	DP	Scissions (mmol/100 g)	Carbonyl (mmol/100 g)	$\Delta$ Carbonyl (mmol/100 g)	Carboxyl (meq/100 g)	$\Delta$ Carboxyl (meq/100 g)
90°C, 50% RH						
0	1653	—	0.29	—	0.57	
72	670	1.10	1.37	1.08		
168	516	1.65	2.06	1.77	0.42	
463	355	2.73	3.15	2.86	0.54	
570	331	2.98	3.45	3.16	0.58	
697	305	3.30	3.50	3.21	0.52	
858	302	3.34	3.91	3.62	0.56	
80°C, 65% RH						
0	1463	—	0.38*	—	0.50	
71	1018	0.37	0.71*	0.33		
239	711	0.89	1.26*	0.88		
407	603	1.20	1.63*	1.25		
575	592	1.24	1.80*	1.42	0.48	
90°C, dry						
0	1653	—	0.29	—	0.53	
169	1368	0.16	0.45	0.16		
463	1033	0.45	0.61	0.32	0.52	
571	986	0.51	0.73	0.44		
697	895	0.63	0.77	0.48	0.51	
858	831	0.74	0.91	0.62	0.52	
1367	682	1.06	1.29	1.00	0.61	
105°C, dry						
0	1379	—	0.44*	—	0.47	—
480	541	1.39	1.59*	1.15	0.42	-0.05
696	494	1.61	1.80*	1.36	0.60	0.13
985	454	1.82	1.93*	1.49	0.67	0.20
1348	424	2.02	2.16*	1.72	0.76	0.29
1805	397	2.22	2.40*	1.96	0.84	0.37
2452	362	2.52	2.69*	2.25	0.99	0.52

\* Average of duplicate measurements

ovens, an increase consistent with an activation energy of about 25 kcal/mol, the same value estimated based on the humid oven degradation rates. Thus, the carbonyl products formed during the cellulose scission and the temperature dependence of the scission rates are consistent with predominantly hydrolytic degradation of this paper, even in the “dry” oven aging.

It is perhaps remarkable that extensive hydrolytic scission should occur in the “dry” ovens even with the low moisture contents of papers under

these conditions. At room temperature and moderate humidity, the filter paper studied here has an equilibrium moisture content of about 7% by weight, or a water concentration of about 400 mmol/100 g of paper. Humid oven aging at 80°C, 65% RH maintains the moisture content of this cotton paper at about 7%,<sup>24</sup> so the hydrolytic scission reaction, which requires one water molecule per scission, can occur with an excess of reactant water. By contrast, dry oven aging at 90–105°C occurs at very low relative humidity in the oven, and the equilibrium moisture content of the paper is consequently very low, much less than 0.5%.<sup>24</sup> Nevertheless, 4 mmol/100 g of scissions, sufficient to cause total strength loss in these papers, can occur with only 0.07% equilibrium moisture content. In other words, extensive hydrolytic scission of the cellulose in the “dry” ovens probably does not require water in excess of the total amount present at equilibrium, and in any case the scissions are produced so slowly that the paper can replenish its consumed water from the ambient humidity in the oven. Rather than being limited by the availability of water, the low degradation rate observed in the “dry” ovens is more likely a result of both the slow transport of reactants and catalysts and the decreased mobility of the cellulose chains themselves, which must contort to achieve the geometry allowing scission to occur.<sup>25</sup> These contortions are believed to be facilitated by the plasticizing effects of the associated water.

If the cellulose scission during the early stage of dry oven aging is, in fact, hydrolytic, then the production of carboxyl groups during the later stage can be taken as evidence of non-hydrolytic chemistry. The slow carboxyl development following an initial slight decrease has been observed in the oven aging of regenerated cellulose<sup>26</sup> and presumably arises from the slow oxidation of carbonyl groups, with some minor loss of the carboxyls initially present through an undetermined degradation route. Since hydrolysis can account for most of the scissions occurring in the dry oven tests, it is unlikely that the chemistries that produce carboxyls are also major pathways for strength loss in this paper, although an indirect contribution, such as exacerbated hydrolysis from the generated acidity, cannot be dismissed.

It is generally assumed that oven aging under low humidity conditions will produce degradation by a different path than in a humid oven. Because water is present in only very low concentrations in paper at low relative humidity, hydrolytic degradation will be slowed, and aging may occur with greater contributions from, or may even be dominated by, other degradation chemistries. In our study of this filter paper, however, hydrolytic degradation seemed to dominate the aging in all of the oven conditions. This may not be surprising, since the filter paper contains measurable levels of

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acid, a catalyst for hydrolysis, and has been purposely freed of metal ion impurities, potential catalysts for oxidative chemistries. The results of humid and dry oven aging for other papers, which may be less predisposed towards hydrolysis, may be different.

### CONCLUSION

The combination of functional group and molecular weight analyses described here offers promise in characterizing the dominant scission chemistry of pure cellulose papers degraded in a variety of environments. Acid treatments produced equal numbers of scissions and carbonyls, the expected "reducing ends" produced by hydrolytic scission. A number of oxidizing treatments of this filter paper have been explored, and a range of degradation paths have been observed. These range from the non-scissioning carbonyl production of periodate treatments to the "random" oxidation of acidic hypochlorite, hydrogen peroxide and near-ultraviolet light. The variety of oxidative degradation suggests that the probability of post-oxidative strength loss, and the efficacy of stabilizing salt treatments, may strongly depend on the nature of the original cellulose oxidation chemistry.

The results of tests on the same papers verify that the degradation chemistry in both humid and dry oven aging is almost exclusively hydrolytic. In the dry oven aging, the rate of hydrolysis is slowed enough to allow observation of contributions from other chemistries which produce carboxyl groups.

This analytical approach holds the most promise in discriminating the dominant degradation path in systems capable of both hydrolysis and oxidation. For example, it is recognized that traces of certain metal ions can catalyze oxidation in paper, but at what concentration do these impurities cause the oxidative degradation to dominate the natural hydrolytic route? In a system where one paper is in contact with another rapidly oxidizing paper, is it the emitted volatile acids or oxidants that control the degradation of the adjacent materials? These and related questions are the subjects of future studies using this method.

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## SUMMARIES

*Determination of the Cellulose Scission Route in the Hydrolytic and Oxidative Degradation of Paper*

The identification of the dominant cellulose degradation chemistry is of central importance to the design of effective paper preservation strategies. In order to discriminate different cellulose reaction paths, chemical analyses were chosen to monitor selectively and quantitatively both the scissions and functional groups produced in cellulose during paper aging. The results for acid-treated paper are consistent with hydrolytic scission, and humid oven aging also seems to degrade the cellulose by hydrolysis reaction. Dry oven aging shows the participation of other chemistries, although the dominant cellulose scission again appears to be hydrolytic. Oxidative treatments produced a variety of degradation behavior, ranging from the "specific" oxidation with periodate (carbonyl production with little chain scission) to the "random" oxidation of acidic hypochlorite and peroxide (3-4 carbonyls per scission). Compared with these "random" oxidations, exposure to near-ultraviolet light seems to be slightly more directed toward chain scission, with relatively little production of oxidation along the chains. These results suggest bounds on the post-oxidation strength loss that will occur due to subsequent "weak link" scission.

*Détermination de l'itinéraire de la scission de la cellulose dans la dégradation hydrolytique et oxydative du papier*

L'identification de la dégradation chimique dominante de la cellulose est d'une grande importance pour projeter des stratégies efficaces pour la préservation du papier. Pour établir les différents itinéraires de réaction de la cellulose, des analyses chimiques ont été choisies afin de contrôler de manière sélective et quantitative les scissions et les groupes fonctionnels produits dans la cellulose au cours du vieillissement du papier. Les résultats pour un papier acidifié sont conséquents avec la scission hydrolytique et le vieillissement artificiel humide semble également dégrader la cellulose par hydrolyse. Le vieillissement artificiel sec montre la participation d'autres chimies, bien que le type dominant de scission de la cellulose apparaît de nouveau être hydrolytique. Les traitements d'oxydation produisent une variété de procédés de dégradation depuis l'oxydation «spécifique» avec périodate (production de carbonyles avec peu de scission de chaîne) jusqu'à l'oxydation «au hasard» (random) d'hypochlorite acide et de peroxyde (3-4 carbonyles par scission). Comparée à ces oxydations «au hasard», l'exposition aux proches ultraviolets semble légèrement plus orientée vers la scission de chaînes. Ces résultats suggèrent des limites à la perte de résistance après oxydation qui se produirait à cause de la scission du point faible.

*Die Vorgänge am Cellulosemolekül beim hydrolytischen und oxidativen Abbau von Papier*

Für die Erarbeitung wirkungsvoller Konservierungsmethoden ist es wesentlich, die chemischen Vorgänge zu erforschen, welche den Abbau von Cellulose ausmachen. Zur Identifizierung der verschiedenen Wege, auf denen Cellulose zu kürzerkettigen Verbindungen abbaut, wurde eine chemische Methode angewandt, mit welcher selektiv und quantitativ die Bildung verschiedener funktionaler Gruppen erfaßt werden kann. Die Zahl der so ermittelten Carbonylgruppen wird in Beziehung gesetzt zum durchschnittlichen Molekulargewicht der Cellulose. Die Ergebnisse beim Abbau von Papieren, die mit Säure behandelt wurden, weisen auf hydrolytischen Kettenbruch hin.

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Auch bei der beschleunigten Alterung in feuchter Atmosphäre scheinen hydrolytische Reaktionen stattzufinden. In trockener Atmosphäre überwiegt die Hydrolyse ebenfalls, jedoch laufen auch andere chemische Vorgänge ab. Oxidation bewirkt mehrere verschiedene Veränderungen: Zum einen die »spezifische«, d.h. die mit Periodat zu erreichende Bildung von Carbonylgruppen verbunden mit Kettenbruch in geringem Ausmaß. Sodann die »durchschnittliche«, erreichbar mit Hypochlorit in saurem Medium und mit Peroxid, d.h. die Bildung von 3-4 Carbonylgruppen pro Kettenbruch. Im Vergleich hierzu scheint der Abbau im kurzwelligem Licht (nahe bei ultraviolett) mehr in Form von Kettenbruch verbunden mit eher geringer oxidativer Bildung von reaktiven Gruppen entlang der Kette stattzufinden. Diese Ergebnisse lassen die Vermutung zu, daß ein Festigkeitsverlust, wie er bisweilen eine Zeitlang nach einer oxidativen Behandlung (Bleichen) auftritt, seine Ursache in Schwachstellen hat, die während der Oxidation gebildet wurden.

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