

Acetylation of cellulose

Another pathway of natural cellulose aging
during library storage of books and papers

Abstract

Historical paper items stored in certain conditions can produce gaseous acetic acid, which speeds up the deterioration of cellulose and leads to a minor level of acetylation in the cellulose material. Surprisingly, this acetylation process occurs naturally without needing a catalyst under standard environmental conditions. Various analytical techniques, including DESI-MS with ^2H - isotopic labeling, have confirmed the presence of organic acetates within paper made from cellulose. Additionally, a Zempel saponification method was effectively used even in the presence of excessive acetic acid and inorganic acetates. This research quantified the impact of acetylation on both model and naturally aged paper samples, unequivocally establishing cellulose acetylation as a significant contributor to paper aging. These findings emphasize the need for further research on acetylation in the context of conservation practices and ideal paper storage conditions.

Introduction

Over many centuries, libraries and museums have played a crucial role in safeguarding a wide array of historical paper artifacts. These precious relics encompass ancient manuscripts, books, and delicate maps, preserving not only the collective wisdom and artistic expressions of past eras but also bearing witness to the relentless march of time. However, lurking beneath their fragile exteriors is a formidable adversary called acetylation, a subtle yet relentless chemical process that poses a significant threat to their preservation.

The aging of paper is a complex journey that historic documents inevitably undergo. As time progresses, various aspects of material aging become evident, leaving their subtle marks on the parchment. Cellulose, the primary component of paper, succumbs to degradation, a process that

unfolds over years, decades, centuries, and even millennia. Two primary mechanisms, hydrolysis and oxidation, play crucial roles in this intricate tapestry of aging, sometimes acting independently and at other times in concert.

The conditions under which paper artifacts are stored, the environmental factors they are exposed to, and the stressors they encounter collectively govern the aging process. Factors such as temperature, irradiation (including UV/VIS, beta- or gamma irradiation), relative humidity or moisture content, exposure to various chemicals, the presence of acids, the existence of metal ions, and fluctuations in environmental conditions all contribute to the ever-evolving state of the cellulose matrix.

Among all the environmental factors influencing cellulose degradation upon natural aging, acids have emerged as significant catalysts for accelerated cellulose deterioration. These acids can either be endogenous, originating from the paper itself, such as acidic degradation products of cellulose or hemicelluloses, or exogenous, introduced by papermaking additives, including alum or resin acids in the case of alum rosin sizing.

The degradation process extends to volatile organic compounds (VOCs), which encompass short-chain ($<C_4$) organic acids, among other organic substances. The detrimental impact of VOCs on cellulose has been extensively explored, primarily focusing on the hydrolysis process and, to some extent, the potential involvement of cellulose oxidation alongside hydrolysis.

In the course of natural cellulose and paper aging, aged paper often becomes more brittle and mechanically unstable, a transformation noted through research. In the presence of gaseous acids, this deterioration is significantly more pronounced than in papers stored under neutral or alkaline conditions. Furthermore, a hydrophilization of the paper surface, impeding the penetration of water or aqueous solvent mixtures during paper conservation treatments, has been

observed. This phenomenon has been associated with a range of chemical reactions, including the conversion of hydroxyl groups to carbonyl groups, the formation of hemiacetal/hemiacetals crosslinks, and the oxidation to carboxylic acids and ester crosslinks. Such surface changes result in varying hydrophobicity levels across the book's cross-section, with central portions being less hydrophobic than margin regions, which are more severely impacted.

Interestingly, hydrophobized surfaces have been observed even in papers without oxidative damage, with the degree of hydrophilization increasing with aging time. This peculiar behavior has piqued the interest of researchers, sparking a quest for a deeper understanding of the underlying mechanisms. This exploration has led to a hypothesis that acetic acid may be involved in acetylating cellulose surfaces, even under conditions typically unfavorable for esterification reactions.

Acetylation of cellulose is a well-established and widely practiced reaction for modifying cellulose, whether on an industrial scale to produce cellulose acetates or on a laboratory scale for analytical or synthesis purposes. This reaction typically requires specific conditions, including the absence of moisture or water and the presence of catalysts, such as concentrated sulfuric acid or other hygroscopic auxiliaries, due to the equilibrium nature of the reaction. In such a reaction, water is thought to favor the reverse reaction, ester hydrolysis, as the equilibrium lies far toward the starting materials' side.

Given the low molar concentration of acids in the storage environment compared to the moisture provided by material and atmospheric humidity, it might be assumed that a non-catalyzed system would not yield significant amounts of organic acetates (esters). However, the hypothesis emerges that acetic acid, under these seemingly unfavorable conditions for esterification, could be capable of acetylating cellulose surfaces. This hypothesis challenges conventional wisdom

and prompts a reevaluation of the observed surface changes and morphological alterations in paper artifacts.

In this current study, we seek to explore the role of (surface) acetylation in the aging of paper and its interaction with acetic acid from both endogenous and exogenous sources. We aim to confirm the presence of organic acetates on cellulose, elucidate the kinetics of acetyl group formation, and ultimately quantify the extent of acetylation. This research delves into the intricate world of cellulose degradation and offers insights that may redefine our understanding of the aging process of historic paper objects.

In essence, the preservation of historic paper objects, those precious vessels of our cultural heritage, demands a holistic understanding of the mechanisms of aging and degradation. Within these delicate pages resides the collective memory of our civilizations, and their conservation is paramount. To safeguard these artifacts for future generations, it is crucial to comprehend the intricate interplay between time, environmental conditions, and the subtle yet potent chemistry of acetylation. Through this quest for knowledge, we embark on a journey to preserve not just artifacts but the essence of history itself, ensuring that the voices of the past continue to resonate in the present and future.

Method

In this extensive research project, a wide array of chemicals was utilized, and various types of paper samples were systematically examined to unravel the effects of exposure to acetic acid on paper aging and preservation. The chemicals employed in this investigation were procured from Sigma–Aldrich–Fluka, situated in Schnelldorf, Germany. These chemicals included acetic acid, β -D-glucopyranoside pentaacetate, dichloromethane, dry methanol, methyl acetate, and a

solution of sodium methoxide. Additionally, an isotopically labeled acetic acid with a 99.5 atom% ^{13}C composition was sourced from Chemotrade, a supplier in Leipzig, Germany. These chemicals were selected for their high levels of purity and were utilized without the need for further purification.

In the course of this research, an extensive range of paper samples, varying in weight from 100 mg to 1 g, were subjected to meticulously controlled aging processes using glacial acetic acid vapor. These aging experiments were carried out under varying conditions, encompassing exposure to different concentrations of acetic acid vapor in a sealed desiccator at room temperature for durations spanning from 3 hours to an extended 42 days. Alternatively, certain paper samples were subjected to aging within sealed ampoules, specifically at an elevated temperature of 70°C .

The selected paper samples represented a diverse spectrum of materials. They included Whatman filter paper, Whatman filter paper deliberately enriched with pigments (such as Cu-acetate and iron gall ink), and samples with the incorporation of binding agents, such as gum Arabic.

Furthermore, linen rag paper samples were used, both with and without the inclusion of gum Arabic as a binding agent.

Following the aging processes, the paper samples underwent a range of post-treatment procedures. Some samples were meticulously washed with deionized water until they achieved a neutral pH, followed by air-drying at room temperature and subsequent storage at -18°C . In contrast, others were promptly stored at -80°C immediately after aging, bypassing the washing phase. These intricately designed experiments, which encompassed diverse paper types, provided valuable insights into the impact of exposure to acetic acid vapor on different paper materials under varied conditions. These findings significantly contribute to our understanding of the

multifaceted processes involved in paper aging and preservation.

To evaluate the consequences of paper storage in acetic acid, a 100 mg sample of Whatman filter paper was carefully placed in a sealed vial, immersed in acetic acid for a duration of four weeks.

The acetic acid in the vial existed in three distinct forms: deuterated acetic acid, non-deuterated acetic acid, and an equal 1:1 mixture of both.

To analyze the effects of this storage, 50 mg segments of each sample were immersed in a 0.1 M aqueous NaHCO_3 solution overnight to neutralize any potential acidity. Subsequently, these segments were rinsed twice with deionized water. The air-dried samples were then thoroughly extracted with chloroform overnight, and the combined extracts were evaporated using nitrogen. The resulting residue was dissolved in a water/methanol mixture and filtered.

For analytical purposes, mass spectra of this solution were recorded using an Agilent 6320 XCT Ion Trap Mass Spectrometer. The analysis was conducted in the positive mode, covering a scan range of 50–500 m/z in profile mode. These procedures allowed for a comprehensive exploration of any molecular changes in the filter paper resulting from its interaction with different forms of acetic acid, offering insights into the impact of acetic acid on the filter paper sample.

The analysis was carried out using advanced equipment, combining an Agilent 7890A gas chromatograph with an Agilent 5975C triple-axis mass selective detector (MSD). This setup featured two distinct inlets: an Agilent multimode inlet and an Agilent split-/splitless inlet.

For the analysis of methyl acetate, a VF-WaxMS column was connected between the multimode inlet and the MSD. The split-/splitless inlet was used for fiber conditioning before enrichment.

To ensure appropriate helium carrier gas pressure, a fused silica capillary was connected to the split-/splitless inlet. The multimode inlet maintained specific conditions and a constant column flow using helium as the carrier gas. The purge flow and injector temperature were also

controlled.

The MSD operated in EI-mode, and data acquisition was conducted in Selected Ion Monitoring (SIM) mode, allowing for precise analysis of methyl acetate and its derivatives.

To prepare for analysis, an internal standard, 4-O-($^{13}\text{C}_2$ -acetyl)-vanillin, was dissolved in methanol. Cellulose or paper samples were placed in vials and treated with anhydrous methanol and sodium methanolate. These samples were then ready for analysis via GC–MS.

In conclusion, this comprehensive research project involved the use of various chemicals and diverse paper samples to investigate the effects of exposure to acetic acid on paper aging and preservation. Advanced analytical equipment and procedures were employed to analyze and interpret the molecular changes in the paper samples resulting from their interaction with acetic acid. This research deepens our understanding of the intricate processes involved in the aging and preservation of paper.

Results

The presence and role of acetic acid in the aging of cellulose, especially in paper, is a complex and important area of study. Acetic acid, which is a type of carboxylic acid, plays a significant role in the aging of paper, particularly in places like libraries, archives, and exhibition spaces where historical documents are stored. It is one of the most common volatile organic compounds (VOCs) found in indoor air, especially in areas where wood and paper materials are prevalent.

Acetic acid can come from various sources, such as wood and plant materials.

One significant source of acetic acid in paper aging is wooden structures often present in storage areas, like solid or particle boards and drawers. In its gaseous form, acetic acid forms dimers by

creating strong hydrogen bonds, resulting in an eight-membered cyclic structure. It's interesting to note that this dimeric structure partially remains intact even when acetic acid turns into a liquid or solid. When acetic acid interacts with mixed liquid or solid phases, these dimers break apart, allowing individual molecules to interact with solid materials. In the presence of water, acetic acid can separate into its acidic components, demonstrating its characteristic acidic properties.

During the process of making paper from pulp, the organic acetates found in the hemicelluloses of wood are intentionally separated. The acetyl groups that are liberated are then converted back into acetic acid for further use. This separation process takes place under specific pH and temperature conditions in commonly used pulping methods, such as the kraft process and the sulfite process. Consequently, the hemicellulose component in the final paper no longer contains its original acetyl groups. Any remaining organic acetates are usually the result of transesterification reactions rather than incomplete initial separation. In contrast, papers made through mechanical or chemomechanical pulping methods tend to retain a significantly higher amount of residual acetyl groups. This difference occurs because the removal of acetyl groups in these methods is less thorough, due to the milder processing conditions involved.

Regardless of whether acetyl groups were initially present in papers or not, cellulose itself can produce small amounts of acetic acid during the aging process. When various cellulose materials undergo aging under specific conditions, a mixture of volatile compounds is generated, with acetic acid and formic acid being the primary components. This aging process is accompanied by the formation of chromophores and the degradation of cellulose chains. The production of these volatile degradation products occurs more rapidly under certain conditions, including acidic, alkaline, or oxidative environments. Cellulose-derived acetic acid results from the hydrolysis

and/or oxidation of cellulose, with the resulting low-molecular-weight fragments serving as precursors for further degradation reactions.

To delve deeper into the process, researchers conducted an investigation to determine whether the generation of acetic acid is related to specific carbon positions within glucose or anhydroglucose units. Different glucoses that were labeled with carbon-13 isotopes were exposed to mild thermal stress, and the resulting acetic acid was analyzed. The findings revealed that all three types of labeled glucoses produced carbon-13-labeled acetic acid, indicating the involvement of various carbon positions in the formation of acetic acid. This observation suggests that the thermal degradation of cellulose is a complex process involving multiple parallel pathways.

Furthermore, the research explored the ability of various carbohydrates and carbohydrate-derived products to produce acetic acid under similar thermal aging conditions. D-glucopyranose was used as the reference substance, and the production of acetic acid from D-fructose and 5-hydroxymethylfurfural (HMF) was compared. HMF, which is a product of hexose dehydration, was identified as the top producer of acetic acid. This suggests that while HMF and fructose may not be intermediates in acetic acid production from glucose, the conditions associated with thermal treatment favor the pathway leading to acetic acid formation. These findings indicate shared degradation mechanisms for acetic acid production during ambient aging conditions.

In addition to these insights, the study explored the possibility of acetylation through gaseous acetic acid under ambient conditions, which closely mimic the conditions of natural aging. Initial experiments were conducted using artificially increased concentrations of acetic acid in the gaseous phase, exceeding the levels typically found in natural storage conditions. These tests confirmed that cellulose acetylation can indeed occur at room temperature and 65% relative

humidity, even in the presence of some water in the pulp. Importantly, this acetylation happened without the involvement of catalytically active strong acids. It's crucial to note that under standard storage conditions in libraries and museums, acetic acid concentrations in the gaseous phase range from 3 to 5 milligrams per liter. This suggests that cellulose can undergo acetylation under these conditions, emphasizing the idea that the acetic acid commonly present in libraries and archives can indeed react with cellulose.

To provide further support for the possibility of cellulose acetylation under real-world aging conditions, the study used isotopic labeling in conjunction with mass spectrometry. This method was used to confirm the occurrence of acetylation in naturally aged paper samples retrieved from libraries and museums. The results showed that cellulose within these samples had undergone acetylation over time. Notably, the degree of substitution (DS) with acetyl groups was found to be quite low. This observation indicates that even in historical books and papers stored for several decades, the extent of acetylation remains minimal.

The research delved deeper into the influence of storage conditions on paper degradation. To accomplish this, four library books dating from 1912 to 1986 were compared to assess the impact of varying storage durations. The degree of acetylation, expressed as DS-Ac, exhibited a range from 0.00007 to 0.03. This means that, on average, there was one acetyl group present within approximately 30 to 14,000 anhydroglucose units in the cellulose. Importantly, the findings highlighted that the degree of acetylation increased with longer storage times. This suggests that the conditions in which materials are stored in libraries play a substantial role in influencing the degradation of paper.

Furthermore, recent research has shed light on the role of surface-confined water within cellulose as a reaction medium. This confined water on the surface is crucial for facilitating reactions that

typically wouldn't occur in bulk water. It plays a significant role in acetylation reactions on cellulose surfaces and significantly impacts the macroscopic properties of cellulosic materials. In summary, acetic acid plays a significant and intricate role in the aging of cellulose, especially in the context of paper. It can originate from various sources, including wood, and, under certain conditions, can lead to the acetylation of cellulose. While the degree of acetylation is generally low, it tends to increase over time in materials stored in libraries and archives. Understanding these intricate processes is paramount for the preservation of historical documents and cultural heritage. Consequently, further research is imperative to explore the specific mechanisms governing cellulose acetylation and its implications for the preservation of paper-based artifacts.