**Kinetic approach to degradation of paper. In situ FTIR transmission studies on hydrolysis and oxidation**

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**Abstract**

This study deals with quantitative and qualitative interpretation of transmission FTIR spectra of aged model paper samples (pure cellulose and cellulose modified with aluminium sulphate) to prepare the basis for a kinetic model of cellulose degradation involving a mixed hydrolytic and oxidative mechanism. The ageing experiments were performed in situ under various conditions (pure water vapour, dried air, 100, 150 °C) to discriminate between hydrolytic and oxidative paths. The focus was on the spectra between 1500-1900 cm⁻¹, where the products of paper ageing appear in the form of various carbonyl groups. A procedure of spectra standardization allowed combining band areas with conversion of carbon atoms in cellulose. From the time evolution of bands the overall kinetic curves were generated and preliminarily analysed. The positions of carbonyl bands were verified by independent experiments. Based on experimental results, a mechanism assuming parallel-consecutive oxidation and autocatalytic hydrolysis was proposed.

1. Introduction

Innocuous and sluggish as it might seem but mischievous as it is, degradation of paper progresses slowly as a flameless fire in libraries. The chemistry behind it is cleavage of cellulose chains caused directly by hydrolysis of glycosidic bonds and also by oxidation of glucopyranose rings. Although the conformation of β-D-glucopyranose polymer is thermodynamically highly stable amongst polysaccharides, aluminium sulphate, a sizing agent added into paper pulp, acting as a catalyst of acidic hydrolysis, is known to have a detrimental effect on the cellulose stability. This is typical of groundwood paper produced over the period between mid-19th and late 20th century, which now represents around 90% of holdings of libraries. The rescue efforts are focused on mass deacidification of those books which are not yet completely degraded and thus on developing and refining the deacidification technologies. The scientific issues that arise with it can be included in three questions:
1. How to describe paper condition?
2. How to estimate paper longevity?
3. What are the long-term effects of various deacidification processes?

The answers may come from resolving the kinetics of cellulose degradation which would combine a mixed-hydrolytic and oxidative mechanism. Presently, paper degradation kinetics is based on the formal rate laws\(^1,2\), which with better or worse results are used to reproduce kinetic curves of accelerated ageing of cellulose.

By and large, paper degradation kinetics is traced by changes in mechanical or physical properties of paper (tensile strength, folding endurance, tear index\(^3,4\), dynamic modulus or mechanical loss tangent\(^5\)) and also by a decrease in polymerisation degree\(^6\). These give rather a bird’s-eye-view of the structural transformations that take place during paper ageing. Notwithstanding numerous examples of the use of vibrational spectroscopy to resolve cellulose structure, crystalline phases\(^7\), hydrogen bond network\(^8,9\), it still seems to have an unexploited potential in the modelling of kinetics of cellulose degradation.

Various sampling techniques have been used so far to study paper materials\(^2\): transmission spectra through KBr pellets\(^10,11\), reflectance spectra using ATR\(^12\), or DRIFT techniques\(^13,14\): each of them, however, suffering from several serious drawbacks. These have also been tested by our group in the first approach to the problem of cellulose degradation\(^15-17\). Preparation of KBr pellets is rather time consuming and not very representative of the environment at which the molecules react and are examined, especially during kinetic experiments. The ATR and DRIFT techniques provide information restricted to the surface region of the samples. DRIFT giving high specular reflection.

This work contributes to the continuing studies on paper degradation kinetics in our group\(^15-17\). Its aim is the preparation of a spectroscopic experimental basis and its qualitative interpretation for modelling of kinetics of paper degradation involving a mixed-control formalism\(^18\). This has been achieved using an in situ FTIR transmission technique. The spectra standardisation problem has been partly solved in our previous paper by using the internal standard (CH stretching band) and by eliminating bound water vibrations at 1640 cm\(^{-1}\) from the spectra\(^17\). Here, our focus is on spectral evolution in the region between 1500-1900 cm\(^{-1}\), where products of cellulose hydrolysis and partial oxidation appear as carbonyl groups of different degrees of freedom.

2. Experimental

2.1 Materials

In this study, unmodified and aluminium-modified paper samples were used. An initial material to prepare these samples was model paper (P1) composed almost of pure cellulose. The model paper was produced from bleached sulphite softwood cellulose (99.5% m/m) related to dry sample; 78 g/m\(^2\); BET surface area: 1.21 m\(^2\)/g obtained from TNO, The Netherlands\(^20\) and recommended as a model material. Its moisture content given by the producer is 7.5% (23 °C, 50% RH). The impurities found in this material were assigned to lignin and oligosaccharides\(^21\).

For the in situ transmission measurements special thin sheets of paper were prepared. The paper pulp was obtained from P1 samples by suspending them in distilled water and further mechanical defibrillation. To prepare Al-modified samples the P1 pulp was immersed into a solution of \(\text{Al}_2\text{(SO}_4\text{)}_3\) of the appropriate concentration. Next, the paper sheets were formed on a sieve. The samples were then dried at 80 °C for 30 min and stored in a desiccator.

The samples of model paper were characterized by pH-contact measurements (TAPPI T 529 om-88) and by atomic absorption spectrometry (AAS). The alcoholic extraction concerning paper grammage, pH and Al content is included in Table 1.

The aluminium content was adjusted to mimic real paper composition. A series of books taken from the collection of the Jagiellonian Library (Poland) from the 80s of the past century were analysed by AAS giving the range of Al content from 0.3–1.1% (m/m).

![FTIR study of paper degradation, e-PS. 2005, 2, 1-12](image-url)
2.2 Apparatus

FTIR spectra were recorded using Excalibur 3000 Digitlab Spectrometer with DTGS detector with an optical resolution of 2 cm\(^{-1}\). The IR reaction cell was situated in the spectrometer sample compartment. The cell was equipped with CaF\(_2\) windows and connected to gas evacuation and supply system. A scheme of the apparatus used is presented in Fig. 1. The cell was heated by an electrical furnace whose temperature was controlled by K-type thermocouples. Overall 128 scans were collected per spectrum.

2.3 Experimental procedures

The procedure of paper ageing was standardized in order to precisely define the reaction initiation and the initial state of the samples. Prior to ageing experiments the reaction chamber with a paper sample inside was evacuated at room temperature for 10 min and then heated up to 100 \(\degree\)C. At this temperature and under dynamic vacuum the paper sample was conditioned for 30 min to desorb bound water. The desorption was monitored by vanishing of the 1640 cm\(^{-1}\) band characteristic of bending vibrations of water molecules.

After the preliminary procedure had been completed, the ageing reaction was initiated by introducing a selected gas mixture (dry air or water vapour) at 100 or 150 \(\degree\)C:
- dry air (AD) - continuously supplied to the reaction cell from the atmosphere through a moisture trap and two zeolitic pumps. The pressure in the chamber was controlled with a manometer to maintain atmospheric pressure (ca. 1000 hPa).
- water vapour (WV) - the reaction cell preliminarily evacuated to 0.1 Pa \((10^{-3}\) Torr) and then continuously fed with pure water vapour from a saturator operating at 20 \(\degree\)C. The pressure of water vapour was controlled by the manometer and maintained at 2.3 kPa (17 Torr).

In some complementary experiments humid air atmosphere (AW) was applied. The evacuated reaction cell was filled with dried air and saturated with water vapour (partial pressure 2.3 kPa) from a saturator thermostated at 20 \(\degree\)C.

Spectra were recorded every 1 h (or 30 min at the beginning of a reaction) at the reaction temperature. It was already proven that collection of the spectra at elevated temperature (<150 \(\degree\)C) has almost no influence both on band shape and on the positions of their maxima\(^{17}\).

3. Results and Discussion

3.1 Spectra standardization

All the spectra presented in this work are pre-processed. The procedure included normalization, water rotational spectrum subtraction, if necessary, smoothing by the adjacent averaging method (no. of points 10) and a baseline correction.

There are two most important problems encountered when a clear interpretation of kinetic experiments is attempted. The first is definition of an initial state of the samples subjected to kinetic experiments ("zero point" on kinetic curves). The second is a proper quantitative interpretation of the physical property measured and undergoing changes with time upon ageing. The physical variable of our interest is the intensity of carbonyl bands in absorbance units.

The first problem has been solved by elaborating the starting protocol of the kinetic experiments which has been described above. The second problem is complex. A consistent and unequivocal interpretation of carbonyl bands is almost impossible when the spectra are collected at room temperature due to the shielding effect of the bend-
ing modes of water molecules adsorbed in paper. Collecting the spectra at elevated temperature allows disposing of water molecular vibrations as it was shown in our previous paper. The interesting issue on water adsorption and desorption is still under study, applying various conditions and using various experimental techniques. In brief, according to our results (FTIR and TG), at an elevated temperature (>70 °C), water desorbs from paper regardless of the gas mixture composition, either under vacuum, in the presence of water vapour (2.3 kPa) or in air (1013 hPa), and does not readabsorb on paper. These findings are illustrated in Figs. 2A and 2B. Upon increasing temperature under vacuum the band at 1640 cm⁻¹ decreased (Fig. 2A) evidencing the completion of water desorption after the sample reached 60 °C. In humid air (AW) introduced to the reaction cell with the P1 sample which underwent desorption in vacuum at 70 °C for 30 min, no increase of the bending vibration mode of water molecules was noted in the spectrum (Fig. 2B).

Another point to discuss is a qualitative interpretation of the observed intensities of carbonyl groups. This is partly overcome by using the in situ method because the signal gathered from the sample comes from the same zone which allows omitting the question of paper inherent inhomogeneity. However, to fully interpret the observed intensities the Beer's law should be regarded:

\[ A_\nu = \log \frac{I_0}{I_\nu} = \varepsilon_\nu(\nu) d\nu \]  

where absorbance of a particular band \( A_\nu \) is proportional to the content \( n_\nu \) of a certain functional group in a certain frequency range from \( \nu \) to \( \nu' \) with the extinction coefficient \( \varepsilon_\nu \) which depends on the frequency.

The extinction coefficient of polarized carbonyl groups (CO2), which is the case of various carbonyl bands occurring upon oxidation or hydrolysis of cellulose, is almost independent of the CO stretching frequency but most of all on the CO groups environment. Thus in the first approach to kinetic interpretation of the spectra we can assume a constant (average) value of extinction coefficient of all carbonyl groups in the range \( \nu \) to \( \nu' \), \( \varepsilon_{\text{CO2}} \). Then the total content of carbonyl groups in the sample, \( N_{\text{CO2}} \), is directly proportional to the integral of absorbance of the overlapped bands in the regarded wavenumber range:

\[ \alpha_{\text{CO2}} = \frac{3}{\varepsilon_{\nu'}} A_{\nu'\nu} d\nu = \varepsilon_{\text{CO2}} \sum n_{\text{CO2}} = \varepsilon_{\text{CO2}} N_{\text{CO2}} \]  

To omit the problem of the wave path length (\( I \)) and paper thickness, all absorbances were normalized using an internal standard elaborated in the previous paper. The area of the CH vibration band (2390 cm⁻¹) of the initial spectrum (namely, the integral in the frequency range 2800-3000 cm⁻¹, i.e. from \( \nu_s \) to \( \nu_s' \)) was the normalization factor for all absorbance values. Note that the symbols std. absorbance or std. integral were used to indicate the normalization performed. The normalization can be expressed by the following equation:

\[ \int_{\nu_s}^{\nu_s'} A_{\nu'} d\nu = \frac{\alpha_{\text{CO2}}}{\alpha_{\text{CH}}} = \frac{\varepsilon_{\text{CO2}}}{\varepsilon_{\text{CH}}} N_{\text{CO2}} \]  

Here, Beer's law was also applied to the CH band.

The conversion of carbon atoms is defined as follows:

\[ X_c = \frac{N_x(0) - N_x(t)}{N_x(0)} \]  

Thus, taking into account that the total content of CH groups from the initial spectrum, \( N_{\text{CH}}(0) \), is approximately equal to the total content of carbon atoms in the initial sample, \( N_x(0) \), we can combine equations (3) and (4) to obtain:

\[ \frac{\alpha_{\text{CO2}}}{\alpha_{\text{CH}}} = \frac{\varepsilon_{\text{CO2}}}{\varepsilon_{\text{CH}}} X_c \]  

Equation (5) is the relation between our observables and the quantity of the species we observed. The standardized integrals (\( \alpha_{\text{CO2}}/\alpha_{\text{CH}} \)) are proportional to the conversion values (\( X_c \)). This relation will be used for kinetic interpretation of the FTIR results.

Alternatively, in another approach a separated carbonyl band from a resolved spectrum (by fitting Gaussian functions) can be used to follow the changes during paper degradation. However, a prerequisite to use this approach is a reliable resolution of bands based on their proper assignment, which requires some further inquiry. Undoubtedly, a benefit of it would be a better approximation of the extinction parameter.

3.2 Carbonyl bands evolution

3.2.1 Time dependence

The experiments were designed in an attempt to discriminate between hydrolysis and oxidation of cellulose and to capture intermediate products of both reactions. At 100 °C and at humid conditions (VW) cellulose is expected to undergo mainly hydrolysis of glycosidic bonds, while in an oxygen rich atmosphere (AD), oxidation of functional groups is presumed to dominate over other reac-
tions. However, under such conditions both reactions should be treated as predominating rather than separate. Oxidation accompanies hydrolysis even in vacuum or in water vapour alone because residual oxygen is always present in paper samples, and conversely, hydrolysis cannot be avoided during oxidation because residual water is present in the paper structure and also because water is a product occurring during paper oxidation. At 150 °C the reaction network becomes more complex: the two reactions are expected to accelerate and to run along with other reactions such as dehydration, autoxidation or transglycosidation. The reaction progress is illustrated by FTIR measurements for pure P1 samples (Fig. 3) and for the samples modified with Al (Fig. 4). For the P1 sample, measurable effects of ageing both in dry air (AD) and in water vapour (VW) were
observed only at 150 °C. At 100 °C, the progress of reactions as traced by FTIR was negligibly small even after 150 h. In the initial spectrum of both samples aged at contrasting conditions (Figs. 3A and 3B) there are residual vibrations of carbonyls present at around 1610 and 1740 cm⁻¹. A certain fraction of them located around 1720 cm⁻¹ evidently comes from the aldehydic terminal groups but the occurrence of the lower frequency maximum may also suggest that the initial P1 samples have already been slightly oxidized. Upon oxidation at 150 °C (Fig. 3A), the intensity of the higher-frequency broad band (1730 cm⁻¹) significantly increases while the intensity of the lower-frequency band (1610 cm⁻¹) remains almost unchanged. The water vapour impact on the P1 paper sample at the same temperature is much less as seen in Figure 3B. The broad band above 1700 cm⁻¹ splits into two maxima at around 1710 cm⁻¹ and 1740 cm⁻¹ whose intensities increase with reaction time.

An addition of a small amount of aluminium sulphate to the paper samples gives rise to a huge acceleration of both oxidation and hydrolysis as seen in Fig. 4 A-D. A reference spectrum of aluminium sulphate solution (0.12 M) used to prepare the modified paper sheets is presented in Fig. 5. In the spectra, region considered by us a fairly broad maximum at around 1600 cm⁻¹ is present both for the modified samples and for the reference solution of Al₂(SO₄)₃. At such a high frequency, water deformational vibrations may arise from H₂O⁺ due to acidic hydrolysis of the salt. The vibrations from hydronium ions remain in the spectra even after sample pre-treatment (vacuum, 100 °C, 30 min) evidencing the presence of acidic centres for hydrolysis.

The general trend with two broad bands developing with time is common for all the Al-modified samples regardless the conditions (AD or VW). However, certain differences in band position and intensity appear in the spectra. In oxidizing atmosphere (AD) at both 100 and 150 °C, profound changes were observed for the band with the maximum at around 1720 cm⁻¹ and much less for that at around 1620 cm⁻¹ (Fig. 4A and 4B). At 150 °C, oxidation was very fast and after 20 h the sample did not show any structure distinguishable in IR spectrum. In water vapour (VW), the higher-frequency band appeared at 1710 cm⁻¹, which is
by around 10 cm\textsuperscript{-1} lower than the frequency evolved during oxidation.

Eventually, using the formalism presented above, overall kinetic curves have been derived from the FTIR spectra of paper aged under various conditions. The standardized integrals ($\alpha_{OCF}/\alpha_{CM}$) of the bands calculated in the broad range (1500-1650 cm\textsuperscript{-1}) which represent conversion of carbon atoms in cellulose ($X_c$) are shown as a function of the reaction time. The kinetic curves obtained in this way from the spectra in Figs. 3 and 4 (samples P1 and P1AI2, respectively) are shown in Figs. 6A and 6B, respectively. Additionally, Fig. 6C presents the results for P1AI3 sample (Table 1) with the highest Al content. The samples are also compared in Figs. 7A and 7B in terms of the Al-content influence the conversion and reaction rate.

An important feature of the kinetic curves is that they start at approximately the same point which validates our standardization procedure (Figs. 6 and 7). According to our results, this point is characteristic of a certain kind of paper, i.e. oxidation and polymerisation stage (number of aldehyde terminal groups).

Comparing the kinetic curves obtained in various conditions we can note the differences in the progress of reactions and their complexity. During preliminary data analysis, various functions were fitted to the kinetic data. A thorough mathematical analysis of the curves is beyond the scope of this paper whose intention was to collect and test the tools for kinetic analysis of paper spectra. Herein we show that the kinetic curves derived from FTIR spectra can be used to tell various reactions apart and to compare ageing progress of papers of various acidity. On the whole, curves obtained in the AD atmosphere were described by a single exponential function. The curves referring to VW conditions are more complex. At 100 °C for the P1AI2 and P1AI3 samples (see curves referring to 100 °C in Figs. 6B and 6C, respectively) the exponential function fits well to the data and thus the kinetics can be approximated by the first-order rate law. This provides evidence that in the presence of water vapour the predominating reaction is hydrolysis. This observation agrees with the Ekenstam equation assuming first order kinetics for hydrolysis of cellulose \textsuperscript{20}. At 150 °C (Fig. 7B), the VW curves cannot be fitted with a single function and therefore reflect a complex reaction pattern involving possible autoxidation or transesterification. The sigmoidal shape of the curve observed for the unmodified P1 sample aged at 150 °C (Fig. 7B) may suggest the autocatalytic character of the reaction for which the acidic centres develop with the reaction time. In Al-modified samples (P1AI2 and P1AI3) the acidic centres are already included in the material and that is why we do not observe the slow initiation. Furthermore, what these two curves have in common is that they show initial acceleration followed by reaction rate stabilisation similarly to the kinetic curves based on DP measurements \textsuperscript{27}.

A strong correlation between Al content in paper (paper acidity, see Table 1) and average reaction rate at 150 °C can also be observed in Figs. 7A and B. The average reaction rate is a slope of the curve measured in a selected period. A stronger (almost linear) correlation can be noted for the reaction carried out in dry air atmosphere than that in water vapour. This indicates that oxidation at 150 °C is accompanied by acid-catalysed hydrolysis which supplies more carbon atoms in glucopyranose rings which are liable to oxidation. In water vapour (Fig. 7B) an initial rate (first 10 h of the reaction) correlates more with Al content than the rate achieved at the stationary state of the reaction (after more than 20 h). This implies that initiation of the reactions taking place in water vapour is influenced by the presence of acidic centres coming from aluminium sulphate.
A more systematic description of the components of a broad and complex band is enabled by fitting of multiple mixed Gaussian-Lorentzian functions. Here it will be used as an outline to discuss band assignment. A detailed discussion on the fitting risk and its ambiguity has been presented in ref. 17. An example of fitting results of the P1 spectrum obtained after 40-h oxidation at 150 °C is envisaged in Figure 8. The prevailing Gaussian character of the bands and their rather significant width indicates the heteromorphic structure of paper material. All in all 9 bands were fitted. The number and positions of fitted peaks were set up basing on the frequencies of the expected products of cellulose oxidation described in the literature19,24,27-29, and on analysis of our spectra (the presence of additional shoulders and maxima). Some of them were verified by independent complementary experiments.

A complex vibrational pattern of various carbonyl groups (cellulose partial oxidation products), still remains the subject of a heated scientific debate. The results on band assignment in the carbonyl region found in the literature are far from being systematic and congruent. For example, Mosini et al.10 and Calvini et al.24 ascribed the two most intense maxima to aldehydic/carboxylic groups (1730 cm⁻¹) and conjugated carboxylic groups (1620 cm⁻¹), despite the fact that in another paper partly by the same authors23, quite reverse band assignment was supposed, similar to that made by Ali et al.12

The position of -COOH stretching mode at around 1740 cm⁻¹ (B3 in Fig. 8) was confirmed by the experiment utilizing acidic groups neutralization with a dilute KOH solution (Fig. 9). The amount of KOH added was adjusted to the amount of carboxylic groups which we could expect in the sample aged under the conditions applied by us (little excess was used). As a result of the reaction with KOH, the broad maximum at around 1730 cm⁻¹ clearly weakened (curve b) and the maximum at 1614 cm⁻¹ was hardly affected. At the same time the sub-bands presumably coming from other intermediate products of cellulose oxidation revealed at 1740 cm⁻¹ and 1710 cm⁻¹. It is worth pointing out that the sample was exposed to the alkaline environment only for a short time at room temperature. However, a series of so-called Lobby de Bruyn-Alberda van Ekenstein transformations, accompanied by β-elimination finally leading to endwise depolymerisation27, may have also occurred. It seems rather doubtful that under the experimental conditions applied, these series of reactions prevailed the neutralisation of COOH groups especially because they did not show any changes in other carbonyl vibrations in the lower frequency range (<1660 cm⁻¹). Thus the assignment of the band at 1740 cm⁻¹ to the COOH

3.2.2 Assignment

Looking back at the spectra collected for two samples treated at various conditions (Figs. 3 and 4) we notice that they consist of many overlapping carbonyl bands seen as satellites or saddles around two main maxima. Indeed, the presence of carbon atoms in various oxygen environments (-COOH, -CHO, -CO) was confirmed by XPS spectra of the C 1s and O 1s electrons obtained for naturally aged samples.10 This is not surprising though, because partial oxidation (a parallel-consecutive type reaction occurring predominantly on C=O groups in glucosepyranose rings) is expected to give a variety of products whose vibrations are tuned by hydrogen bonds network also undergoing changes with time. This is the reason why characteristic group vibrations may appear at the frequencies higher than typically described in the group frequencies databases. This also explains the shift of the two main bands within around 5 cm⁻¹ with the reaction time under certain conditions.
vibrational modes seems quite rational. Additionally, it supports the consecutive character of the presumed oxidation mechanism: unquestionably, the vibrations at around 1740 cm\(^{-1}\) representing the final oxidation stage of carbonates in glucopyranose rings increase with time.

It may also be assumed that these vibrations come from ester groups which can arise at such a position of the spectrum and may form in the reaction of carboxylic groups with unreacted alcoholic groups. The neutralization experiment cannot fully exclude their formation since the observed decrease of the 1730 cm\(^{-1}\) mode might be due to the shift in the equilibrium between esters and carboxyls. However, this hypothesis is rather weak since, firstly, the P1 paper is acidic (Table 1) and, secondly, there are no additional COS vibrations from esters which should appear below 1400 cm\(^{-1}\). The latter was proved by an ageing experiment performed under rough conditions (AW, 150 and 250 °C) to observe the final and immediate ageing effects (Figs. 10A and 10B). As a reference, an initial spectrum obtained after sample pre-treatment at 100 °C is also included in Fig. 10. No new COS vibrations evolve in the range below 1400 cm\(^{-1}\), which is visible both on the direct spectra (Fig. 10A) and on the difference spectra (Fig. 10B). All we can discern is a decrease in the intensity of various bands observed in the OH bending and CH deformation zone (between 1400 to 1200 cm\(^{-1}\)) and in the associated ring vibrations zone (below 1200 cm\(^{-1}\)).

With regard to positions of other bands, the vibration mode observed at around 1710 cm\(^{-1}\) (B4 in Fig. 8) can be attributed to aldehydic groups since it evolves in the presence of water vapour at various temperatures (Figs. 3B, 4C and 4D). Aldehydic groups appear on opening of the terminal pyranose rings in cellulose chains which is favoured by temperature. A low amount of the presumed aldehydic groups formed during oxidation of P1 at 150 °C (Fig. 8) is in accordance with the presumed consecutive character of oxidation. Moreover, the aldehydic group on the C(6) carbon atom on the glucopyranose ring, which we would expect to form, has a rather low probability of occurrence.

We cannot provide a direct evidence for positions of other bands yet, however, the resistance of the 1506 cm\(^{-1}\) mode to the oxidation (B7 in Fig. 8), as observed for the P1 sample (see also Fig. 3A), may suggest that it originates from conjugated ketonic groups at positions 2 and 3 in the glucopyranose rings. A similar tendency with time is exhibited by the band at around 1645 cm\(^{-1}\) (B6 in Fig. 8) which can be assigned to enolic group \(\text{\textit{co}}\), a carbonyl group tautomer. Another possible configuration of carbonyl groups, \(\text{\textit{co}}\), could be attributed to the band at 1680 cm\(^{-1}\) (B5 in Fig. 8) similar to quinone-type vibrations described by Agarwal\(^{19}\). Other less intense vibrations supposedly come from the P1 sample impurities. Among them, the bands at 1550 and 1510 cm\(^{-1}\) (B6 and B9) are said to be characteristic of the lignin present in the sample\(^{16,19,24}\), which was found in limited amount in P1 samples\(^{21}\). The monoketonic group - a carbonyl band with the largest number of degrees of freedom - is the most difficult to grasp.

### 3.2.3 Reaction network

The observations made during kinetic studies on paper degradation using transmission FTIR in situ technique are summarised in the reaction network including simultaneous oxidation and hydrolysis of cellulose which are supposed to proceed at temperatures not higher than 100 °C (Fig. 11). At higher temperatures the reaction scheme would have to include dehydration, condensation or

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**Figure 10A:** FTIR in situ spectra of the initial P1 sample pre-treated at 100 °C (i) then aged in dry air for 2 h at 150 °C (a) and at 250 °C (b). Changes in original spectra upon oxidation.

**Figure 10B:** FTIR in situ spectra of the initial P1 sample pre-treated at 100 °C (i) then aged in dry air for 2 h at 150 °C (a) and at 250 °C (b). Difference spectra obtained by subtracting the initial spectrum from the spectra of oxidized samples (a-i) and (b-i).

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transglycosidation reactions but this would have to be confirmed by independent experiments and, in fact, is not the case of routine paper ageing experiments usually performed at lower temperature range to prevent other cellulose degradation paths. Hence, the reaction model we search for, should cover the lower temperature range to mimic the conditions at which paper materials are stored and degrade.

The mechanism presumed combines the parallel-consecutive character of oxidation and autocatalytic path represented by hydrolysis. Structural units of our interest that undergo various changes, are functional groups located on the glucopyranose monomer. These are also our observables in the IR spectra. Thus in the course of the combined reactions, carbon atoms occupying various positions in the ring (denoted as C(1), C(2), … C(6) in Fig. 11) loose their identity, gradually transforming into various carbonyl groups of different degrees of freedom, namely ketonic, aldehydic and carboxylic groups. These were detected as fairly broad and overlapping bands in FTIR spectra. The probability of occurrence of a certain path in the reaction network must be estimated by additional kinetic experiments leading to determination of the corresponding rate constants. For example, the fact that C-OH from C(2), C(3) and C(4) atoms are the most prone to oxidation can be included in the mechanism assuming a high rate constant for the paths starting from these atoms.

In the discussed mechanism, hydrolysis is indicated by splitting of the hemiacetal bond, between two glucopyranose rings, C(1)-O-C(4). The terminal rings, as it was hinted above may open, giving rise to the cleavage of C(1)-O-C(5) bond in the same ring and to the formation of CHO groups. On opening the ring, the C(5)OH groups formed become available for oxidation. The formation of COOH groups - the final product of cellulose partial oxidation - enables another catalytic path of hydrolysis involving protons.

Such a mechanism in the form of reaction steps will be the basis for a mass balance of the system, which can be used to derive a kinetic equation.

4. Conclusions

An in situ FTIR technique has been proven to give reliable data for the study of kinetics of paper degradation through hydrolytic and oxidative paths. The spectral analysis involved both qualitative interpretation of the observed intensities of carbonyl vibrations and carbonyl band assignment. To obtain kinetic curves of the degradation, our effort was focussed on standardization of the spectra, which included:
- selection of a model paper for kinetic studies,
- selection of the spectral region for kinetic interpretation between 1500-1900 cm\(^{-1}\) where carbonyl groups occur,
- elaboration of the experimental kinetic protocol with a particular stress on the determination of an initial state of the samples,
- removal of water bending modes by collecting the spectra at an elevated temperature,
- normalisation of spectra using an internal standard (CH 2900 cm\(^{-1}\) band of an initial sample),
- relation of the Lambert-Beer’s law to the conversion of carbon atoms in cellulose.

In order to discriminate between oxidation and hydrolysis, the contrasting reaction conditions were chosen: dried air or water vapour, various temperatures, various amounts of Al added to model paper samples (P1). The reactions were regarded as predominating under the selected conditions.

The overall kinetic curves obtained show the differences in the degradation progress with time under various conditions. Their most characteristic features are as follows:
- All kinetic curves started at the same initial conversion value which is characteristic of a paper type and its initial oxidation and polymerisation stage;
- At lower temperatures (100 °C) hardly any changes in the time frame up to 150 h were observed for model paper samples P1 irrespective of the ageing atmosphere used. Al-modified P1 samples give much higher conversion than pure P1 samples. In water vapour the kinetic curves can be described by first order kinetic equation typical of hydrolysis.
- At higher temperatures (150 °C), in water vapour atmosphere, a complex reaction pattern was exhibited by all the samples. For the P1 samples, the sigmoidal shape of kinetic curves can be accounted for by the autocatalytic character of hydrolysis. For the Al-modified samples a short fast acceleration period is followed by a constant degradation rate. In contrast, monotonous increase in the conversion was observed in dry air.
- The correlation between Al content in paper (paper acidity) and the reaction rate under various conditions was also demonstrated. A strong influence of Al content on oxidation rate at 150 °C implies that it is accompanied by acid-catalysed hydrolysis which supplies new centres for cellulose oxidation.

The carbonyl band assignment was supported by complementary results which allowed distinguishing carboxyl and aldehyde vibrational modes as arising at around 1740 and 1710 cm⁻¹, respectively. These also showed the most profound changes with time upon ageing under various conditions.

All our findings are supportive of the parallel-consecutive mixed oxidation and hydrolysis mechanism involving autocatalytic path for hydrolysis.

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References

List of symbols

\( A \) - absorbance
\( \alpha \) - standardized integral of bands
\( l \) - wave path length
\( e \) - extinction coefficient
\( e_{av} \) - average extinction coefficient
\( \lambda \) - wavenumber
\( n \) - content of a functional group in cellulose, moles or molar fraction
\( M \) - total content of functional groups of a certain kind, moles or molar fraction
\( X \) - conversion

Subscripts

CO - carbonyl group
CH - methyldyne group
U - carbonyl units in cellulose
fl - type of carbonyl group
\( j,k,\ell \) - integration limits