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Chemiluminescence - A Novel Method in the Research of Degradation of Paper. I. The Effect of Light on Stacked Sheets of Paper

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Summary: Statistical scission of cellulose macromolecules leading to the negative changes in mechanical properties of the paper has been quantified on irradiated stacks of newsprint papers. Attention has been paid to comparison of changes occurring in respective sheets of the stack. The correlation of the results of non-isothermal chemiluminescence method from which the rate constant of paper oxidation has been determined for 105 °C with the changes of carbonyl groups concentration, pH and double folds has been outlined.

Keywords: carbonyl concentration; cellulose; chemiluminescence; double folds; lignin; paper degradation; pH of paper; rate constant of oxidation

Introduction

The degradation of paper is determined by the degradation of its components such as cellulose, lignin, hemicellulose and various additives which may affect the paper stability in a more or less predictable way. The reduction of the molar mass of predominating component - cellulose - may take place either through a cationic mechanism or as a free radical process with an intervention of oxygen, humidity and additives.[1] The additives modify not only the chemical reactivity but also the physical state of the paper including T_g of cellulose and its crystallinity. This may have a direct effect on the facility of oxygen and other reactants diffusion to potential reaction sites.

Deacidification of acid papers is a generally accepted methodology of the prolongation of their remaining service life. It eliminates a hydrolytic mechanism of the main chain scissions initiated by acid sites. By this mechanism terminal semiacetal groups are formed which are the sites of predominant attack of oxygen. The degradation of cellulose is an example of a counterplay between both the ionic and free radical mechanism which may have the different significance in the overall process depending particularly on temperature.[2]

In spite of the fact that the techniques used for the characterization of paper degradation are numerous there still exists an open space for application of more sophisticated methods which may throw more light on the particular significance of both mechanisms.

Recently[3–9] a potential of the chemiluminescence method which monitors the light emitted from the surface of oxidized paper has been underlined. The light originates from free radical recombination of peroxyl radicals and/or from decomposition of hydroperoxides which are formed during cellulose oxidation.

Present paper submits an examination of individual sheets in irradiated stacks of newsprint paper, both the original and deacidified by methoxy methyl magnesium carbonate. The stacks of paper sheets represent the behaviour of the book under real conditions of irradiation.

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The results from non-isothermal chemiluminescence were compared with double folds endurance tests, with the determination of initial concentration of carbonyl groups and with pH of the sample extracts.

Lignin is a particular reactant in the paper as it introduces new chromophores to the system. Radical scavenging properties of lignin and its antioxidant action in free radical oxidation of hydrocarbon polymers at one side and easy formation of superoxoanion radicals under alkaline conditions and the sensitivity of the lignin to the light at the second side indicate that despite of numerous papers published until now,[10–18] the proper mechanism of its action during paper degradation is very complex.

The blends of pure crystalline cellulose and alkali lignin were prepared and their stability has been examined by chemiluminescence and thermogravimetry in order to assess the role of lignin in thermal oxidation of cellulose.

Experimental Part

Samples

Papers examined were newsprint paper made in Větřní, 2003, Czech Republic. Paper was denoted as V. The composition: 64% - mechanical wood pulp bleached by sodium dithionite, 13% - nonbleached sulphite pulp, 13% - bleached sulphate pulp, retention agent Polymin SK, starch. Paper is not sized, its weight is 45 g/m^2, ash residue 10%, kaolin 10%, brightness ISO 70%, pH 4.0, pH measured 6.7, sheet thickness 0.073 mm.

Lignin, alkali, low content of sulfonate, $M_n = 10000$ and $M_w = 60000$ g/mol was purchased from Aldrich.

Microcrystalline cellulose (powder) for thin layer electrophoresis, DS-0 was purchased from Fluka.

Samples Preparation

Control Samples of Paper

were immersed into methanol, p.a. grade, for 10 minutes, dried in the air and flattened in bookbinding press.

Preparation of Methyl Methoxy Magnesium Carbonate (MMMC)

20 g of Mg shavings (Kovohuty Istebne, Slovakia) was dissolved under reflux in 1 l of absolute methanol. The system was bubbled through by carbon dioxide until Mg and Mg methanolates were completely dissolved. Deacidification solution originally containing 10% vol. of MMMC was diluted by methanol to 2% which corresponds to 0.8 mol/l of MMMC.

The solution of MMMC in methanol was characterized by infrared spectrum from Infrared spectrophotometer Perkin Elmer 599. The reference solvent was methanol.

Deacidification

was performed by immersion of paper samples 10 minutes into 2% solution of MMMC in methanol and dried on air. The papers were flattened in bookbinding press. The samples were denoted as VD.

Stacks of Papers

From papers V and VD the stacks having 50 sheets were prepared. Half of the stack was protected by a neutral book board (samples $V_{control}$ and $VD_{control}$) the half was irradiated by the day light (samples V_{irr} and VD_{irr}). The light has absorption curve corresponding to the window glass with transmittancy from 320 nm. Paper stacks were irradiated at the inside part of the window for 144 days. After each 7 days the position of the respective samples was changed. The position of a respective sheet in the stack is numbered from the top of the stack.

Measurements

Carbonyls Concentration

was determined by the hydrazine method according to Albertsson and Samuelson[19] adopted for the small weight of sample. Only carbonyls bound to cellulose were determined in such a way. The average value was determined from 3 parallel measurements.

Double Folds
were determined according to Schopper (modified ISO 5626, 1993 for small sizes of paper). Load on springs was 0.28 kg. The average value was determined from 12 parallel measurements. The standard deviation was + − 21%.

pH
was measured in water extract from paper of magnitude 3 × 1 cm in 2 ml of deionized water obtained by 1 hr heating at 100 °C. pH was measured on Sentron Argus (The Netherlands) pH meter with an electrode Sentron ISFET Hot-Line. The average value was determined from 4 parallel measurements. The standard deviation was + − 11.7.

Chemiluminescence (CL) Measurements
were carried out on the luminometer Lumipol 3 produced at the Polymer Institute of SAS, Bratislava. The intensity of emitted light (in counts/s) was recorded under non-isothermal conditions as the records of intensity vs temperature. The rate of heating was 2.5 °C/min. The instrument dark count rate was 2–3 counts/s.

Samples of the initial weight (around 4 mg) were placed on aluminum pans of the diameter 9 mm and put into the oven of the CL apparatus; the gas flow above the sample was 3 l/h.

Thermogravimetry
was carried out using Mettler-Toledo TGA/SDTA 851^e thermobalance in nitrogen and oxygen atmosphere (30 ml/min) in the temperature range 25–500 °C and at the heating rate 5°/min.

Results and Discussion

The effect of the position of paper sheet in the stack on the light emission registered in chemiluminescence - temperature runs for several samples V is seen in the Figure 1. Top irradiated sheet V1 has the lowest chemiluminescence intensity and the chemiluminescence intensity - temperature curve shows the sigmoidal shape with an inflexion point at about 150 °C. Deacidified

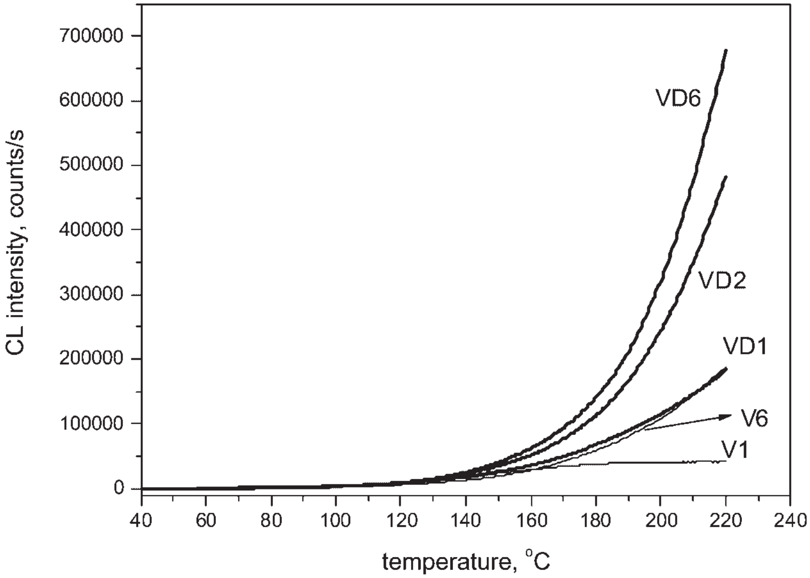


Figure 1.
Chemiluminescence intensity – temperature runs for several irradiated samples of papers V and VD. The rate of heating 2.5 °C/min, oxygen atmosphere. The numbers denote the position of respective sheet from the top of the stack.

samples VD give significantly more intense chemiluminescence signal which is probably related with the more intense chemiluminescence process of terminal groups oxidation occurring in the presence of magnesium ions. No inflexion point can be achieved with deacidified samples within the temperatue interval studied which indicates that these samples are more stable towards oxidation than irradiated top sheet of the original stack.

The ageing of the samples due to the light is always accompanied by the reduction of pH and by changes of other parameters characterising the resulting quality of the paper. Figure 2 shows that pH is the lowest for the top sheet of an irradiated stack and increases with the sequence number of the sheet from the top of the stack. Figure 3 shows that the double folds have the lowest rating for the top sheet of an irradiated stack. When going down from the top in the stack of paper the mechanical stability of the paper sheets in irradiated stacks increases.

Quite an interesting correlation shown in Figure 4 between the chemiluminescence intensity recorded at 220 °C and initial pH of respective sheets exists indicating that the acid samples give lower light emission when compared with deacidified ones. The loss of alkaline reserve may be explained by the oxidation of carbon 6 on cellulose backbone which is obviously rather slow process at low temperatures and starts to be important at temperatures above 100 °C.

For all samples examined we have determined the averaged rate constant of the paper oxidation at 105 °C which is the usual temperature of estimation of thermal stability of paper. The methodology of the rate constants determination is described elsewhere.[2]

As it may be seen from the Figure 5 the increasing rate constant of the paper oxidation indicating its lower thermo-oxidation stability correlates quite well with the number of double folds. This is very promising result regardless of the fact that the number of double folds depends not only on the chemical state of the material but also on the residual content of water and of other additives while the chemiluminescence rate constant reflects

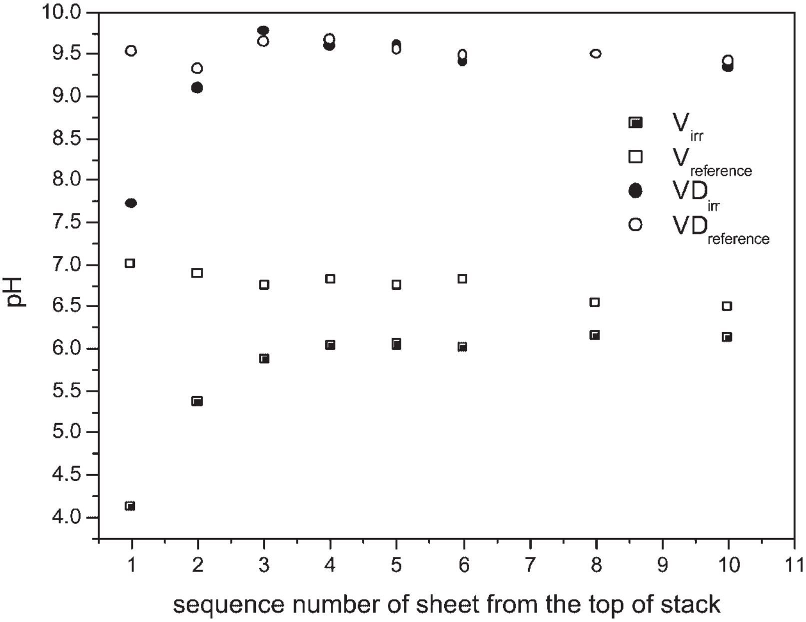


Figure 2.

pH of extracts for a respective sheet of paper V and VD in stacks upon irradiation (full points). Non-irradiated samples V and VD are represented by empty points.

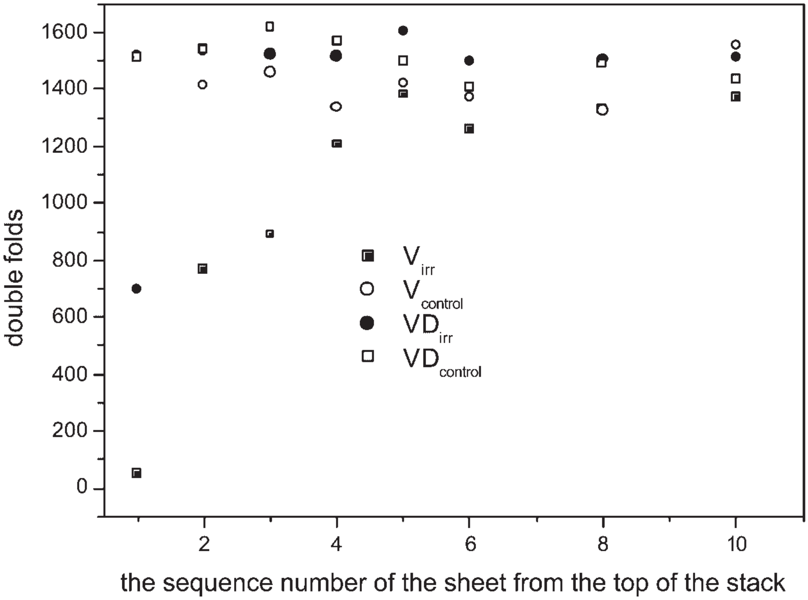


Figure 3.
Double folds of irradiated samples V and VD (full points). The control samples V and VD are represented by empty points.

the integral behaviour of the paper material.

An important parameter having the effect on chemiluminescence intensity is the initial concentration of carbonyl groups which act not only as destabilizing moieties in cellulose but they are also the potential light emitting groups.

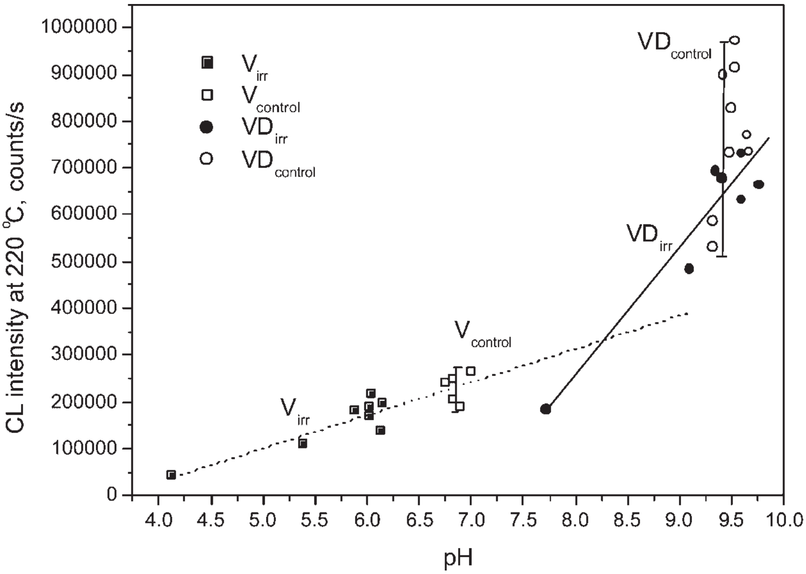


Figure 4.
The plot of chemiluminescence intensity at 220°C on initial pH for irradiated (full points) and control samples (empty points) V and VD. The rate of heating 2.5 °C/min., oxygen.

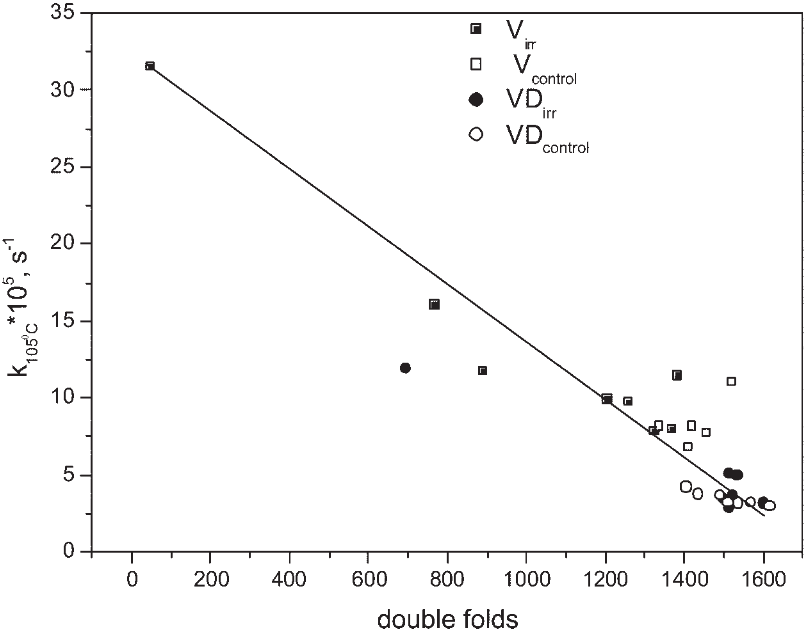


Figure 5.
The correlation between double folds of irradiated (full points) and control samples of the papers V and VD and the rate constant of paper oxidation determined from non-isothermal chemiluminescence runs for 105 °C.

Figure 6 demonstrates how the rate constant of oxidation of papers of samples V and VD is related to the amount of carbonyls. It may be of interest that both the rate constant and concentration of carbonyls decrease with the increasing sequence number of the paper sheet from the top of the stack.

The role of lignin in oxidation of paper has been examined on the mixtures of powders of microcrystalline cellulose and alkali lignin which were prepared in a laboratory mixer and chemiluminescence and thermogravimetry runs were performed in oxygen under the linearly increasing temperature. From the results demonstrated in Figures 7 and 8 it may be seen that alkali lignin contributes to the destabilisation of the cellulose in the paper significantly. This is demonstrated not only by chemiluminescence experiments where chemiluminescence – temperature runs for the samples containing increasing concentration of lignin are shifted to lower temperatures, but also by thermogravimetry curves where volatile products from the mixture of both components are formed at lower temperature than those from samples without lignin. Oxidation of lignin with oxygen at temperatures from 20–170 °C in the samples which are initially alkaline is accompanied by the formation of singlet oxygen O_2^* which may be the reason of an increased chemiluminescence intensity (Figure 7) at lower concentrations of lignin. The reduction of the light emission at high concentration of lignin in the mixtures with cellulose will be mainly due to the fact that the samples become black and an extensive absorption of the emitted light occurs.

On the basis of above experimental results, the stoichiometry of the reaction for cellulose may be depicted in the Scheme 1.

The process has free radical character being initiated by free radicals P which appear in the paper due to thermally induced reactions or by trace amounts of metal ions present in any paper. One cannot exclude even direct interaction of cellulose with biradical of oxygen in its ground state The sequence of reactions

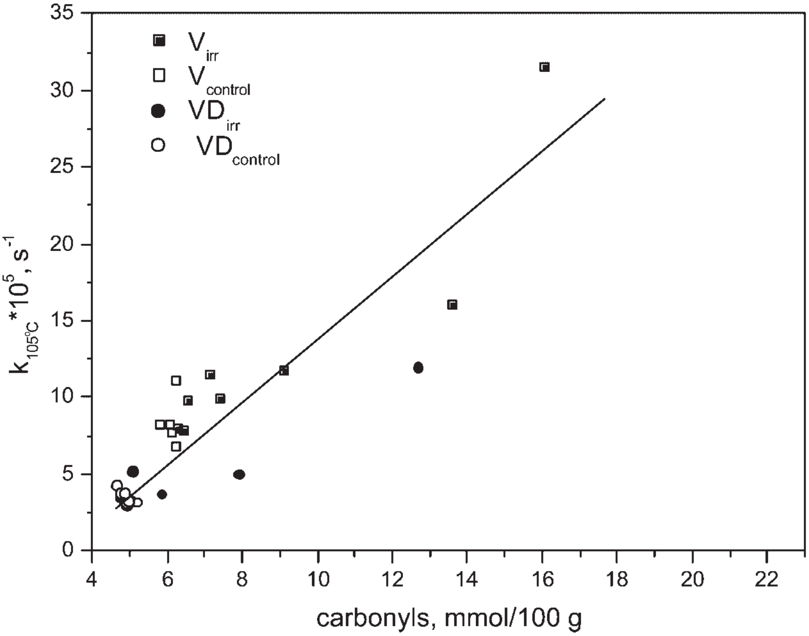


Figure 6.

Correlation between the initial concentration of carbonyls in irradiated (full points) and control (empty points) papers V and VD and the rate constant of papers oxidation determined from non-isothermal chemiluminescence measurements in oxygen for 105 °C.

which ultimately may lead to chemiluminescence is shown below (Scheme 2).

The most probable elementary step from which chemiluminescence is emitted is disproportionation of secondary peroxyl radicals which are formed on carbon 6 of glucopyranosyl unit. According to the Russel scheme[20–22] of disproportionation

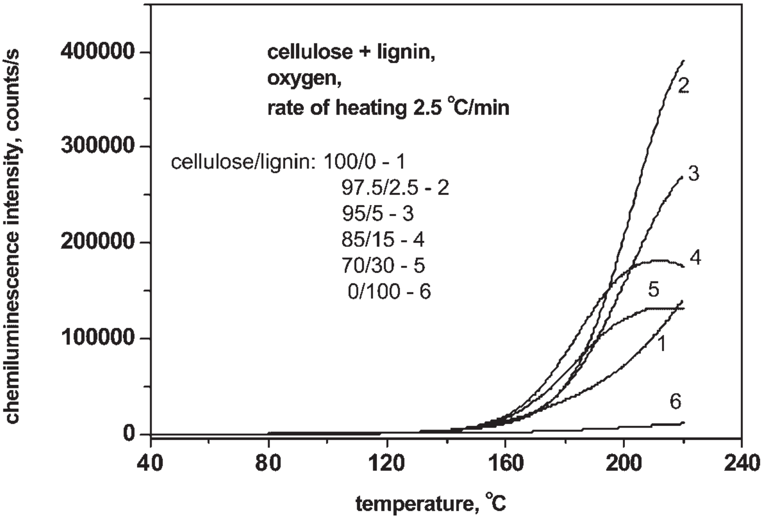


Figure 7.

Chemiluminescence – temperature runs for the mixtures of microcrystalline cellulose with alkali lignin. Oxygen atmosphere, the rate of heating 2.5 °C/min. The composition of the mixture is expressed in part/part mass ratio.

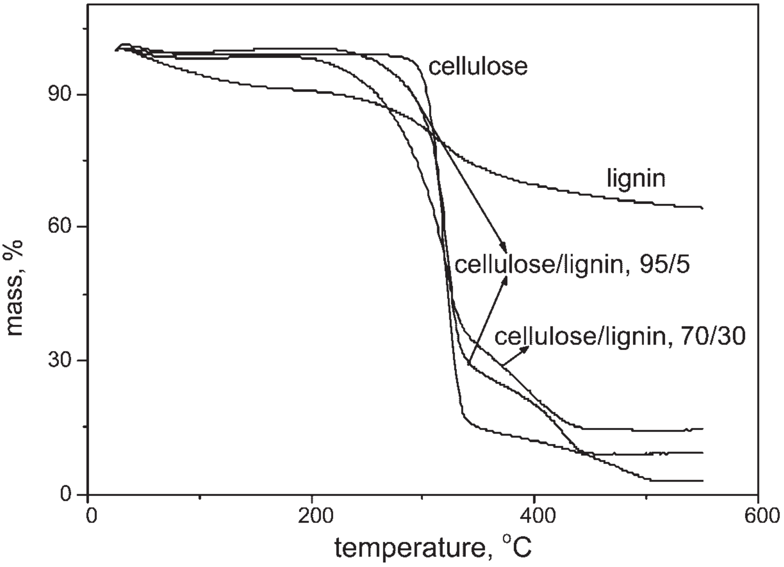


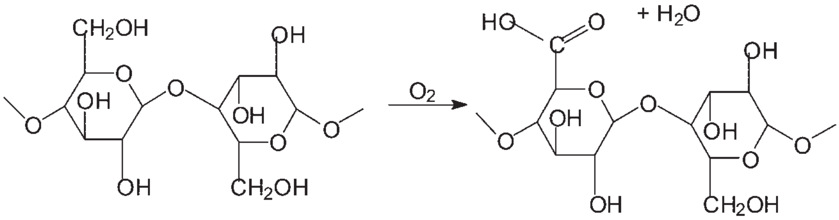
Figure 8.
Non-isothermal thermogravimetry runs for mixtures of microcrystalline cellulose with lignin in oxygen. The rate of heating 5 °C/min. The composition of the mixture is expressed in part/part mass ratio.

of secondary peroxyl radicals derived from C6 atoms of cellulose units it may be seen that carboxylic acid, excited triplet of aldehyde, singlet oxygen and water are formed almost simultaneously. The simultaneous formation of carboxylic acid and water may lead to a subsequent heterolytic cleavage of C-O-C bonds linking glucopyranosyl units.

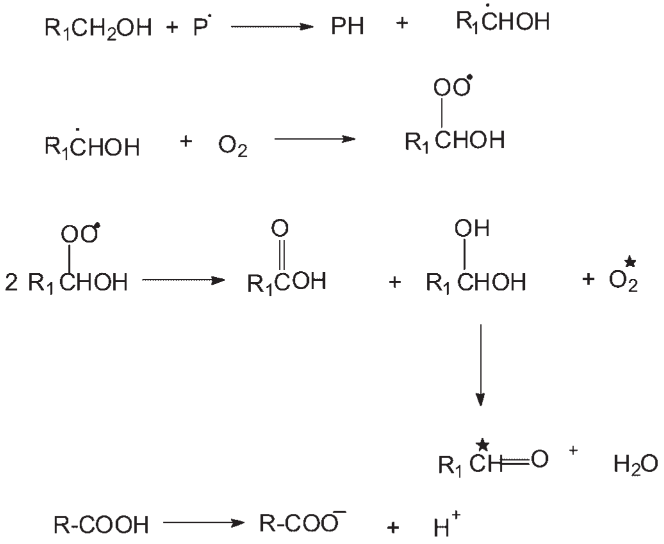
Peroxyl radicals which are potentially formed on carbons 1, 2, 3, 4 and 5 of glucopyranosyl unit are tertiary peroxyl radicals which in their recombination give oxygen and two oxyl radicals or dialkyl peroxide, respectively, probably without observable light emission.

Of importance seems to be the understanding of a significant increase of chemiluminescence when MMMC is added to paper samples. Initial pH of the papers at the presence of MMMC is between 8.5 and 9.5. The alkaline reserve of the paper is represented by MgO which remains in the paper after its thermal treatment. The significant increase of the light emission was also observed when cellulose was treated with magnesium carbonate.[7] Provided that calcium carbonate giving also pH around 9 is used instead of magnesium salt no increase of chemiluminescence above the reference level was observed.[7]

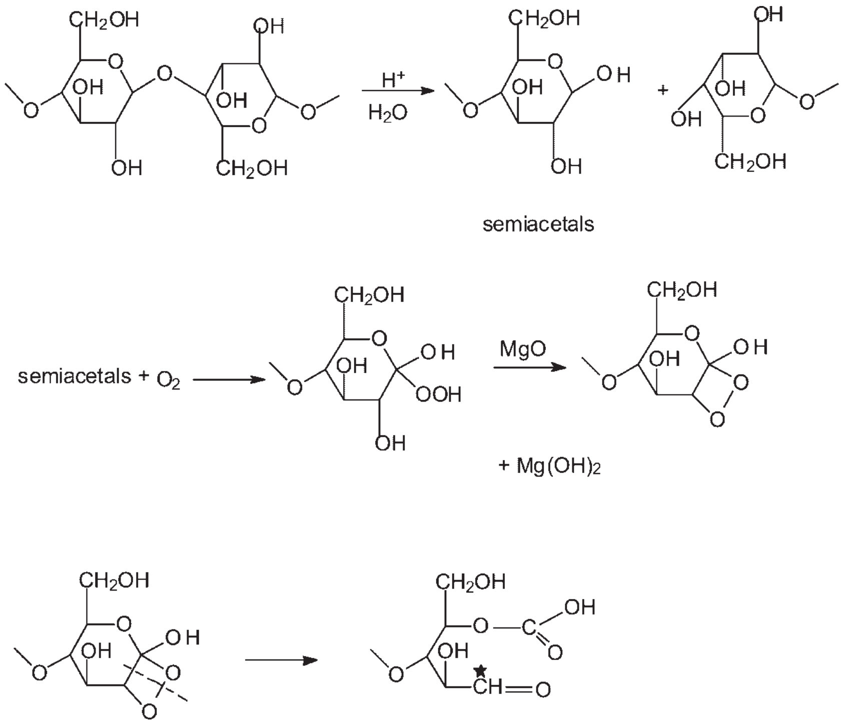
These facts together with an easy peroxidation of terminal aldehydic groups (semiacetals) in cellulose tend us to consider chemiluminescence reaction which has a considerably higher quantum yield of light emission than disproportionation of secondary peroxyl radicals (Scheme 3).



Scheme 1.



Scheme 2.
Asterisks denote the excited states of aldehydes and oxygen which emit the chemiluminescence upon conversion to their ground states.



Scheme 3.
Asterisk denote an excited state of the molecule providing the light emission.

The decomposition of intermediate dioxetanes which are probably formed from terminal β-hydroxy hydroperoxides in the presence of MgO seems to be quite realistic scheme. Analogy with the synthesis of a relatively stable tetramethyl dioxetane prepared from corresponding β-bromohydroperoxide in the presence of alkaline Ag_2O suspension[23] may be put forward in support of such a hypothesis.

Conclusions

Non-isothermal chemiluminescence experiments, double folds tests, pH and carbonyl groups concentration changes in sheets of irradiated stacks of paper indicate that the penetration of the incident light leading to the harmfull effect on the paper properties is extended almost to the 5th sheet from the top. The loss of alkaline reserve in deacidified irradiated samples of papers may be explained by the oxidation of carbon 6 of glucopyranosyl unit of cellulose leading to the formation of carboxylic acid groups.

The chemiluminescence method appears to be a very good tool for investigation of paper oxidation. The correlations of the rate constants of paper oxidation determined from non-isothermal chemiluminescence experiments for 105 °C and oxygen atmosphere with double folds, concentration of carbonyl groups and pH loss for control and deacidified papers are very promising for the larger application of the method by archivist and conservators of historical documents based on paper.

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