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Thermal oxidation of cellulose investigated by chemiluminescence. The effect of water at temperatures above 100 °C

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Abstract

The kinetic data obtained from chemiluminescence (CL) accompanying oxidation of cellulose containing pulps were compared with those from polymerization degree determinations and mechanism of CL accompanying the oxidation of cellulose was discussed. At the same time, the CL method has been used to explore the effect of oxygen and water in a reactor allowing the humidity control. The specially designed chemiluminometer Lumipol 3 has been used for this purpose coupled with humidity control chamber. An addition of water flow to oxidized pulp sheet leads to an immediate increase of CL and to its relaxation decay. The similar phenomenon has been observed when water flow was stopped, the decay of the signal following the initial increase, however, occurred with slower kinetics. The signal increase due to wetting and drying was strongly pronounced by the presence of $Mg(HCO_3)_2$ and by the origin of the pulp sheet, and in the case of wetting, also by the total amount of water being in contact with the surface of pulp sheet.

Keywords: Cellulose; Thermal oxidation; Humidity; Chemiluminescence

1. Introduction

Cellulose belongs to relatively stable polymers with respect to thermal oxidation when compared, e.g. with polyolefins, however, the mechanism of its degradation is much more complex. Heterochain character of the macromolecular backbone and the presence of hydroxyl groups in its structure brings about the vulnerability of materials containing cellulose towards the effect of ionic reagents—in acid mode cellulose degrades relatively fast by a cationic mechanism. The free radical pathway of degradation is typical for cellulose in an alkaline environment due to e.g. Ca or Mg carbonates impregnation (Kolar, 1997). The complexity of the mechanism is brought about by the superposition of radical and ionic degradation taking place to a different extent in dependence on conditions of sample exposition.

The kinetics of the process is affected by temperature, oxygen and also air humidity. The latter case is of particular interest for free radical mechanisms. Kleinert and Marraccini (1963) have shown that ageing of bleached pulps below 100 °C in the presence of high humidity results in higher values of peroxides formed. It can be presumed that water starts to support chemical reactions in cellulose bringing about the adequate mobility of polymer segments, solvation of low molar mass species and dissociation of ionic compounds (Vittadini, Dickinson, & Chinachoti, 2001).

Oxidation of cellulose by oxygen may start at different sites of 1,4-β glucopyranosyl monomer unit of cellulose chain. As Shafizadeh and Bradbury (1979) proposed, the preferred sites of the primary oxygen attack are carbon atoms in positions 1 and 4 of glucopyranosyl units, but an attack focused on carbon atoms 2 and 3 linked with alcoholic groups and carbon atom at the position 5 linked

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with methylhydroxyl group cannot be excluded either. The dependence of the oxidation pattern may also be affected by structural defects like carbonyl groups, etc. inherently present in cellulose structure (Malešic, Kolar, & Strlič, 2002; Strlič, Kocar, Kolar, Rychlý, & Pihlar, 2003). The kinetic length of the oxidation chain for cellulose is rather short, i.e. the level of hydroperoxides attained is much lower than that in the case of polyolefins under comparable conditions (Kolar, 1997). Typical autoacceleration of the oxidation reaction due to hydroperoxides as observed for polyolefins was not observed during the progress of the cellulose oxidation. As shown in paper by Malešic et al. (2002), the initiation of oxidation may be focused also on carbonyl groups.

In this report, we present the latest results on chemiluminescence (CL) from cellulose and cellulose-containing materials accompanying their oxidation in and without the presence of water, which could contribute to the clarification of the reaction mechanism leading to the emission of CL.

Two independent routes of investigation of the above systems may be depicted. The first, which is oriented towards the search of the relation between CL emission and the essential changes in the material under investigation is supported by our last paper (Rychlý, Strlič, Matisová-Rychlá, & Kolar, 2002) where the average rate constants of oxidation determined from non-isothermal CL runs for pure cellulose in oxygen were shown to be comparable with those determined from the decrease of polymerization degree (DP). The second route may involve the investigation of the effect of large set of additives on CL from cellulose in order to find additives with potential applicability in more efficient stabilization towards degradation of paper based 'information supports'.

2. Experimental

2.1. CL measurements and samples used

The CL experiments were carried out on Lumipol 3 chemiluminescence instrument produced at the Polymer Institute, Slovak Academy of Sciences, Bratislava (www.polymer.sav.sk). For the investigation of the effect of water on CL from oxidized cellulose, Lumipol 3 has been interfaced with a specially designed mixing reactor enabling the measurement of CL from circular areas (7 mm in diameter) of whole sheets of a polymer in a non-destructive way. In such a way, paper based historical artefacts and even pages from the whole books can be examined at low temperatures. Experimental conditions during the respective measurements are indicated at each Figure.

The following samples were used in this study: Whatman (Wh) filter paper No. 1 (Maidstone, UK), cotton (C) pulp sheets (Radeče, Slovenia) and bleached sulphate (SA) pulp sheets (Pöls, Austria). Whatman filter paper is regarded as pure cellulose, all other materials like SA (sulphate bleached pulp) and C (cotton) papers are pulp sheets.

When preparing the sheets of paper with different additives, usually 5×10^{-3} M solution of an additive in water was used, the paper kept there for 30 min at room temperature and then dried in vacuum at room temperature.

The degree of polymerization (DP) was determined according to a standard procedure described elsewhere (SCAN-CM, 1988).

2.2. Simple model of the degradation process

The kinetic model of cellulose degradation which has been the subject of numerous papers (Ekenstam, 1963; Emsley, Heywood, Ali, & Eley, 1997) is quite simple, however, it enables the time and/or temperature dependence of the process to be quantified and may be useful in extrapolations of kinetic data to lower temperatures or in comparing the effect of the different additives. Polymerisation degree (DP) is understood here as the ratio of concentration of monomer units (N) to polymer molecules (i) as follows:

$$\mathrm{DP} = \frac{N}{i} \tag{1}$$

The concentration of polymer molecules increases in time due to degradation and decays due to crosslinking. Provided that the process is taking place statistically, the kinetics of the increase of concentration of macromolecules (for the case of degradation) may be described by equation:

$$\frac{\mathrm{d}i}{\mathrm{d}t} = mki^n \tag{2}$$

where n stands for the order of main chain scissions and $m=1$ for the case of degradation and $m=-1$ for the case of crosslinking. The most frequent reaction orders encountered in the literature are $n=0$ or 1.

For the case of $n=0$ and $m=1$:

$$\frac{\mathrm{d}i}{\mathrm{d}t} = k \quad \text{and} \quad i = i_0 + kt \tag{3}$$

where i_0 is initial concentration of macromolecules in the system. For DP we have:

$$\mathrm{DP} = \frac{N}{i_0 + kt} \tag{4}$$

or

$$\mathrm{DP} = \frac{\mathrm{DP}_0}{1 + \frac{k}{i_0}t},$$

where

$$\mathrm{DP}_0 = \frac{N}{i_0}$$

and after transformation:

$$\frac{1}{\mathrm{DP}} - \frac{1}{\mathrm{DP}_0} = \frac{k}{i_0 \mathrm{DP}_0} t \tag{5}$$

or

$$\frac{\mathrm{DP}_0}{\mathrm{DP}} = 1 + \frac{k}{i_0} t \tag{6}$$

The Eq. (6) gives the rate constant k/i_0 of magnitude s^{-1} which makes possible a direct comparison between samples of different initial DP.

To develop some methodology of CL data classification, we have to understand the reactions leading to the light emission. Chemiluminescence generally expresses the rate of sample oxidation, its intensity depending on the set of parameters such as the geometry of the sample, temperature, oxygen concentration, the concentration of potential emitters, like carbonyl groups in the sample, morphology and water content, etc. One has to be aware that oxidation may ultimately lead to (a) degradation, i.e. reduction of molar mass or (b) to crosslinking with increase of average molar mass, or (c) transformation of side or terminal groups while molar mass remains unchanged.

Any of the above cases, which can be mutually interrelated, may occur in the case of cellulose oxidation. Let's assume that the CL intensity I is proportional to the rate of DP decrease:

$$I = \mu \left[-\frac{\mathrm{dDP}}{\mathrm{d}t} \right] \tag{7}$$

μ stands here for the proportionality constant. If it is the case, the kinetic parameters obtained from the CL and DP determinations should be comparable.

According to Eq. (6)

$$-\frac{\mathrm{dDP}}{\mathrm{d}t} = \frac{k}{i_0 \mathrm{DP}_0} \mathrm{DP}^2$$

and for non-isothermal conditions we have:

$$-\frac{\mathrm{dDP}}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{A \exp(-E/RT)}{i_0 \mathrm{DP}_0} \mathrm{DP}^2 \tag{8}$$

T is temperature, A and E is pre-exponential factor and activation energy of corresponding Arrhenius' temperature dependence of the rate constant k and $\mathrm{d}T/\mathrm{d}t = \beta$ is the constant rate of sample heating.

After integration of Eq. (8) and substitution into Eq. (7) it may be received for non-isothermal conditions:

$$I = \mu \frac{A \exp(-E/RT)}{i_0} \frac{\mathrm{DP}_0}{\left[1 + \frac{A}{\beta i_0} \int_{T_{\mathrm{room}}}^{T} \exp(-E/RT)\mathrm{d}T\right]^2} \tag{9}$$

Similarly as in our last paper (Rychlý et al., 2002) the CL process was considered to be governed by two independent kinetics, faster and slower. For such a case the Eq. (9) may be rewritten as follows:

$$I = \sum_{i=1}^{2} \frac{P_i}{\left[1 + \frac{A_i}{\beta i_0} \int_{T_{\mathrm{room}}}^{T} \exp(-E_i/RT)\mathrm{d}T\right]^2} \tag{10}$$

where P_i is the proportionality constant including the corresponding terms from the Eq. (9) and $i = 1$ and 2 corresponds to the faster and slower process of cellulose oxidation, respectively.

It is of interest that while the process of the chain scission has the character of the zero order, the CL runs formally correspond to the second order scheme.

3. Results and discussion

3.1. Comparison of non-isothermal CL and isothermal DP measurements

The principal differences in non-isothermal CL runs from different pulps sheets are seen in the Fig. 1. SA pulp gives the most pronounced light emission signal related to 1 mg of the sample, while CL records for cotton pulp and Whatman cellulose are lower. The samples were kept in oxygen and heated by the rate 3 °C/min from 40 to 220 °C. Each line in Fig. 1 is the average of three parallel runs.

The parameters of Eq. (10) determined from experimental runs by non-linear regression analysis for 3 examined samples are summarized in Table 1. Agreement of the theoretical fits with experiment is very good, indeed (Fig. 2). Averaged rate constant k_{av} were introduced for comparison with DP experiments were defined as follows:

$$k_{\mathrm{av}} = \frac{P_1}{P_1 + P_2}\frac{k_1}{i_0} + \frac{P_2}{P_1 + P_2}\frac{k_2}{i_0} \tag{11}$$

Here k_1/i_0 and k_2/i_0 are rate constants of faster and slower process, respectively, which for a given temperature were

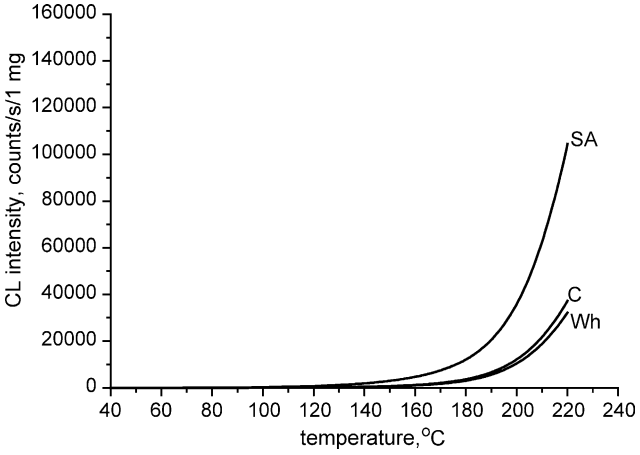


Fig. 1. Comparison of non-isothermal CL runs for oxidation of different papers, oxygen, the rate of heating 3 °C/min, (each curve is an average from three parallel runs).

Table 1
Parameters of Eq. (10) found from non-isothermal runs in oxygen for Whatman (Wh) cellulose and SA and C pulp sheets

Paper	Faster process			Slower process		
	P_1 (counts/1 mg)	A_1/i_0 (s^{-1})	E_1 (J/mol)	P_2 (counts/1 mg)	A_2/i_0 (s^{-1})	E_2 (J/mol)
C	2.43×10^6	4.06×10^3	58 141	1.3×10^8	1.34×10^{10}	128 409
Wh	1.13×10^6	$5.35\ 10^4$	64 327	1.11×10^8	9.85×10^9	126 951
SA	6.31×10^7	1.19×10^3	60 083	1.9×10^8	4.38×10^{12}	149 775

calculated from parameters in Table 1. Comparison has been done with results obtained from the slopes of DP_0/DP vs. time plots taken from paper by Zou, Uesaka, and Gurnagul (1996) (column a in Table 2) and from our own measurements at 90 °C (Fig. 3, row b in Table 2), both sets of experiments were in air. The results of paper by Zou et al. are related to bisulfite bleached pulp.

As it may be seen in Fig. 3, plots DP_0/DP vs. time are showing also two regions of decomposition, faster and slower. Two kinetic regions of degradation of examined samples were also observed in the higher temperature region (from 120 to 220 °C) for SA pulp sheets in oxygen. Comparison of rate constants of faster and slower process determined from non-isothermal CL for SA pulp in oxygen is shown in Table 3 and in Fig. 4. It may be thus concluded that the assumption expressed by Eq. (7) appears to be correct and that the kinetics of degradation examined either by non-isothermal CL measurements and DP measurements is consistent. At the same time, one should be aware of the fact that isothermal CL experiments show much more complex pattern of oxidation which was not de-convoluted properly until now (Rychlý et al., 2002).

The pre-requisite of the 'apriori' introduction of faster and slower process is based on observation of departure from the straight line in experimental course of CL intensity vs. temperature. (Fig. 5) plotted in Arrhenius' coordinates. This departure occurs around 170 °C and as shown in Fig. 6 it corresponds to the change from the decaying to the increasing character of the isothermal light emission which follows after each increase of temperature.

This is in agreement with the abrupt start of the mass loss measured by thermogravimetry during the oxidation of cellulose initiated by periodate (Kumar & Yang, 2002) or with the position of the breaking point in the plot of paper strength vs. temperature of the preceding degradation (Hill, Lee, Darvenira, & Saha, 1995).

The similar increase in the slope of Arrhenius' plot when coming from low temperature to higher temperature degradation region in the case of synthetic polymers is usually explained by an increase in mobility of macromolecular chains occurring around glass transition temperature (T_g) of polymer. In the case of cellulose, T_g is situated at considerably higher temperature (around 250 °C) and its pronounced shift to lower temperatures due to the presence of water was not confirmed by DSC measurements. From measurements of temperature dependence of dielectric properties, the so-called σ-transition (Einfeld, Meissner, & Kwasniewski, 2001) appears to be responsible for this declination which is situated around 170 °C. The σ-transition appears to be related to the migration of protons in cellulose. Together with the maximum of dielectric losses at this temperature, there occurs also a sharp increase of electric conductivity (Ali, Emsley, Herman, & Heywood, 2001; Yousef, Shabaka, Nada, & Abd El Nour, 1991). From spectral measurements of thermally treated cellulose, a reduction and subsequent increase of crystallinity takes place in this temperature region (Imai, Putaux, & Sugiyama, 2003; Zugenmaier, 2001). Taking into account that there are macromolecules of monoclinic and triclinic crystalline phase in cellulose micro-fibrils which have a different thermodynamic stability, one can assume that the rearrangement and shift in crystalline phase after scission of a certain critical amount of hydrogen bonds will occur above some temperature. The change in the position of macromolecules in the crystalline phase may directly lead to the transfer of some segments from crystalline into amorphous phase which may have impact on increase of reactivity, proton migration and other properties.

3.2. Effect of water gas on chemiluminescence

Fig. 7 shows the isothermal course of CL at 150 °C in and without the presence of water during the thermal oxidation of a sample of Whatman cellulose containing $Mg(HCO_3)_2$. Typical for such runs is an immediate increase of the light

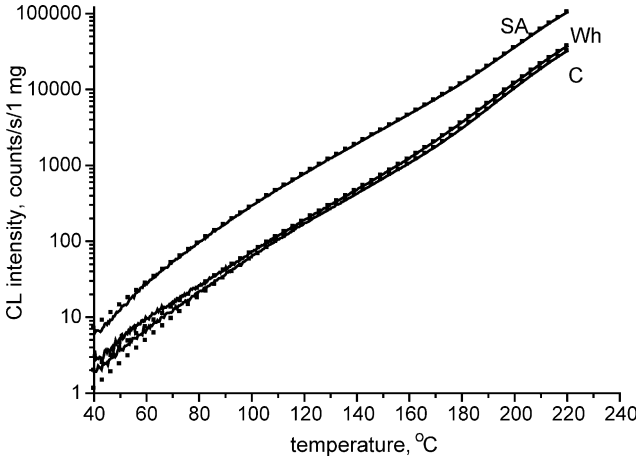


Fig. 2. Experimental runs and theoretical fits from chemiluminescence measurements corresponding to Fig. 1. Points are values fitted by means of Eq. (10). and Table 1.

Table 2
The average rate constants found according to Eq. (11) for oxidation of Whatman cellulose, C and SA pulp sheets for temperature region from 60 to 100 °C

Temperature (°C)	Samples			
	Wh	C	SA	(a)
60	5.1×10^{-8}	6.4×10^{-8}	1.3×10^{-7}	5.0×10^{-8}
70	1.0×10^{-7}	1.2×10^{-7}	2.4×10^{-7}	1.6×10^{-7}
80	1.9×10^{-7}	2.1×10^{-7}	4.4×10^{-7}	3.9×10^{-7}
90	3.5×10^{-7}	3.5×10^{-7}	7.7×10^{-7}	1.2×10^{-6}
90 (b)	From 5.4×10^{-7} to 1.4×10^{-7}	4.1×10^{-7}	From 3.0×10^{-7} to 1.2×10^{-7}	
100	6.27×10^{-7}	6.2×10^{-7}	1.3×10^{-6}	2.9×10^{-6}

The column (a) refers to the value found from paper Zou et al. (1996) from DP determinations.

emission when water is added. This increase lasts several seconds only and it is followed by a fast decay. The phenomenon was reported first by Kelly, Williams, Mendenhall, and Ogly (1979) and confirmed in our paper (Strlič, Kolar, Pihlar, Rychlý, & Matisová-Rychlá, 2001). The hypothesis may be put forward that the increase of CL signal due to the water admission may be brought about by mechanical scissions of the bonds in the main chain due to water molecules penetrating into the polymer mass and by the subsequent recombination of formed free radicals. However, in such a case one should expect that there will not be so strong an effect of the initial quality of the pulp sheet. The intensity of the signal is much stronger in the case of SA pulps and/or samples containing $Mg(HCO_3)_2$ when the pulp is essentially alkaline (Fig. 8). Also Whatman and cotton pulps with an addition of magnesium carbonate give a much more pronounced signal peak as compared with Whatman or cotton pulp sheet without any additive. Of interest is also the fact that the increase of CL intensity above the original value (CL peak) depends on the time of preceding sample drying as well as on the overall amount of water being in contact with cellulose (Fig. 9). It is thus more probable that addition of water facilitates the motion of free radicals which in recombination reactions provide the emission of the light. The question remains how these free radicals are being generated on the cellulose surface and what is their nature?

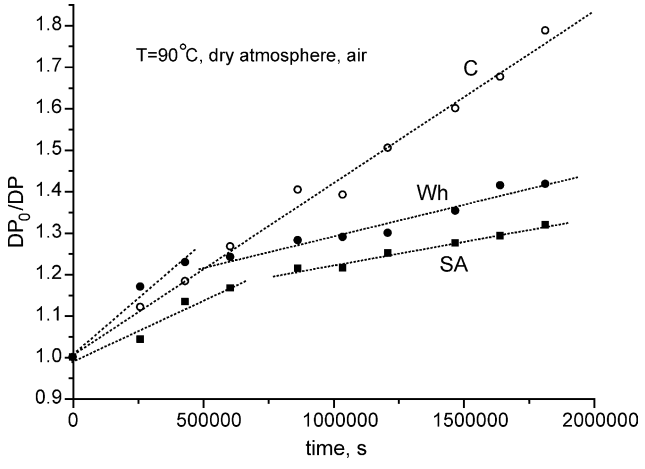


Fig. 3. DP_0/DP plots for cotton (C), SA pulps and Whatman (Wh) cellulose at 90 °C in dry atmosphere of air. Two slopes are typical for faster and slower process as observed also by chemiluminescence.

An interruption in water supply which is connected with an increase of oxygen concentration being in contact with cellulose surface is accompanied by an immediate CL growth as well, however, it is not as sharp as in the case of water addition. The sensitivity of the light emission towards the concentration of oxygen in the surrounding medium was already documented by the Fig. 5. Loss of water from the cellulose structure may alternatively contribute to the increase of the internal tension in the sample due to motion of macromolecular chains to thermodynamically favorable positions and to formation of intermolecular hydrogen bonds between cellulose segments which will substitute those with water.

3.3. On the origin of chemiluminescence from oxidation of cellulose

The important dependence of CL signal on the concentration of oxygen in surrounding atmosphere confirms an assumption that the light emission is provided by the recombination of polymer peroxyl radicals which are formed in free radical oxidation of cellulose. This was accepted in oxidation of hydrocarbon polymers (Ashby, 1961; Audouin & Verdu, 1987; Billingham, Then, & Gijsman, 1991; George, 1981; Forstrom & Terselius, 2000; Matisová-Rychlá & Rychlý, 1996; Zlatkevich,

Table 3
The values of rate constants for the limiting cases of faster and slower process as determined for SA pulp sheets from DP determinations and non-isothermal chemiluminescence runs in oxygen

Temperature (°C)	DP measurements, k/i_0 (s^{-1})		Non-isothermal CL measurement, k/i_0 (s^{-1})	
	From	To	From	To
120	1.6×10^{-6}	6.0×10^{-7}	1.1×10^{-5}	6.2×10^{-8}
140	8.7×10^{-6}	2.2×10^{-6}	2.8×10^{-5}	5.6×10^{-7}
160	3.1×10^{-5}	9.6×10^{-6}	6.3×10^{-5}	4.2×10^{-6}
180	1.3×10^{-4}	4.0×10^{-5}	1.3×10^{-4}	2.6×10^{-5}
200	3.0×10^{-4}	4.5×10^{-5}	2.6×10^{-4}	1.4×10^{-4}
220	5.1×10^{-4}		4.7×10^{-4}	6.3×10^{-4}

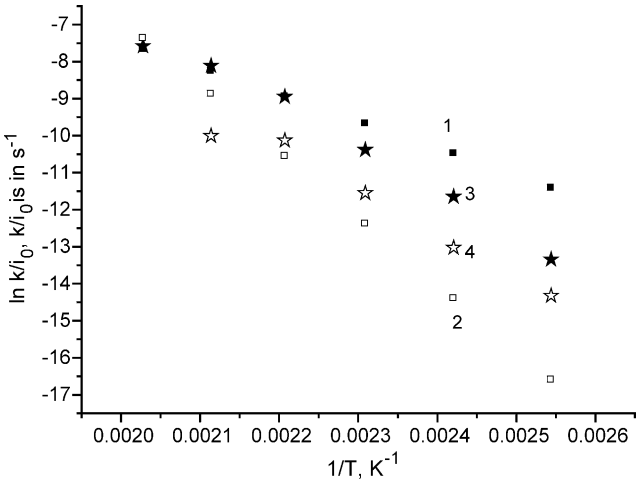


Fig. 4. Upper and bottom values of k/i_0 constants related to faster and slower process from non-isothermal chemiluminescence measurement (points 1 and 2) and from DP decay (points 3 and 4), SA pulp, oxygen, the temperature interval 120–220 °C.

1989) and it appears that it may be valid also in oxidation of cellulose. The elementary reaction of peroxyl radical disproportionation is sufficiently exothermic to be able to transfer the potential emitter of the light (carbonyl groups, oxygen) into an excited state. The development of the CL signal in time and temperature may be at the same time related with the development of various hydroperoxide levels in the system under investigation. In the case of cellulose, however, hydroperoxide groups bound to the tertiary or secondary carbon atoms of macromolecular chain and hydrogen peroxide which is formed from superoxide anions may play an important role in initiation of oxidation particularly at reduced temperatures and in the presence of water. Indeed, as proposed previously (Thornalley & Stern, 1984), the formation of hydrogen peroxide is supposed in the mechanism of atmospheric oxidation of aldehyde groups and it was also confirmed by the data in paper by Kolar (1997).

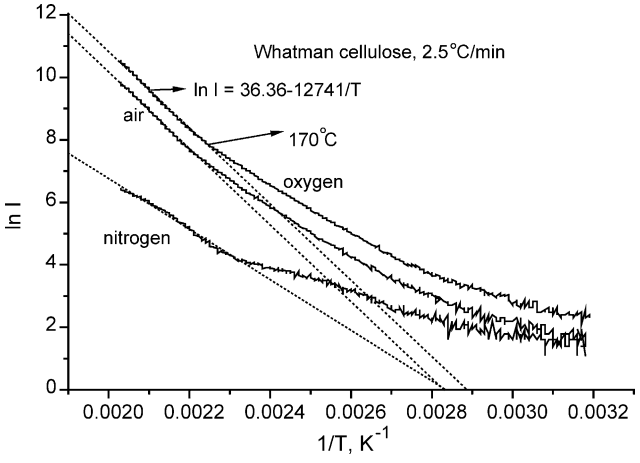


Fig. 5. Arrhenius' plots of chemiluminescence intensity for oxidation of Whatman cellulose in different atmospheres.

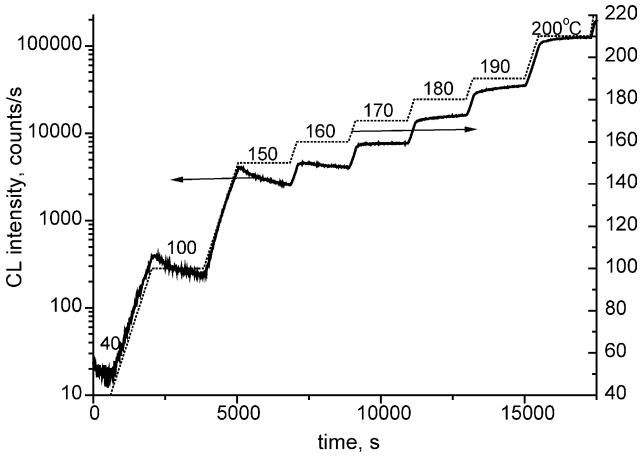


Fig. 6. The stepwise heating of Whatman cellulose in oxygen; temperature is increased from 40 to 200 °C by the rate 2.5 °C/min and then sample is kept at a given temperature for 30 min.

The existence of correlation of CL non-isothermal kinetics with the kinetics of decrease of polymerization degree under comparable conditions indicates that CL phenomenon should be related to main chain scissions in cellulose. This could be possible for the case of disproportionation of unequal peroxyl radicals, one being tertiary peroxyl radical situated at position 1 and 4 of glucopyranosyl unit while his partner should be primary or secondary peroxyl radical or hydrogen peroxyl radical.

To understand the relaxation phenomena connected with the admission of water and subsequent drying of the cellulose sample we have to take into account the pronounced effect on CL emission from pulp sheets of some cations like magnesium especially in alkaline environment (Fig. 8). From the literature data, magnesium ions are attached to hydroxyl groups of one monomer unit while calcium ions which are rather inefficient in promoting CL signal will link hydroxyls from different monomer units of cellulose. This is in accordance with the finding that calcium promotes dimerization of bone osteocalcine while

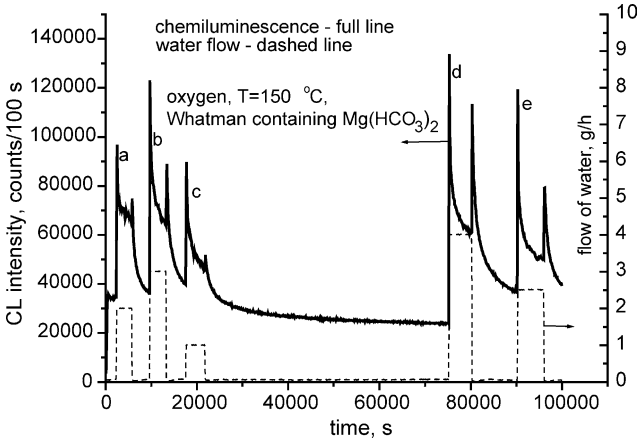


Fig. 7. Changes of chemiluminescence intensity for Whatman cellulose containing $Mg(HCO_3)_2$ in oxygen after admission and removal of water at 150 °C, chemiluminescence runs—full line, water flow—dashed line.

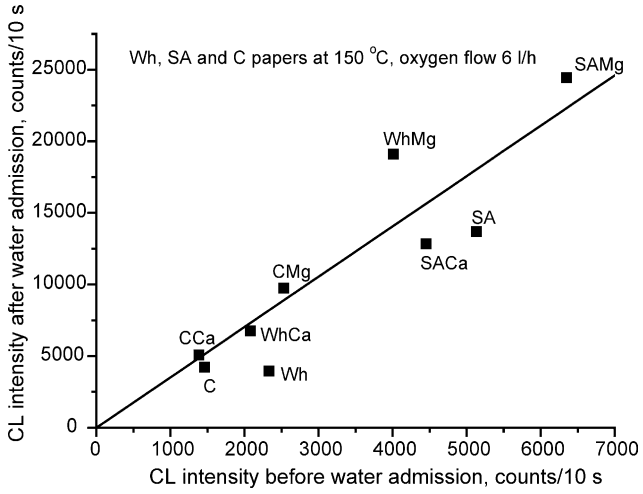


Fig. 8. The correlation of increase of CL intensity after water admission with initial level of chemiluminescence emission for Whatman (Wh) cotton (C) and sulphate bleached pulp SA impregnated by $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$—samples are designated by corresponding element of cation.

magnesium does not, both cations being bound to the same extent (Nousiainen, Derrick, Kaartinen, Maenpaa, Rouvinen, & Vainiotalo, 2002). At the same time Mg^{2+} ions have been reported to promote significantly the electron transfer from (TPP) Co—tetraphenylporphyrin cobalt—to p-benzoquinone while no reaction takes place in the absence of Mg^{2+} ions in acetonitril (Fukuzumi & Ohkubo, 2000; Ohtsu et al., 2000). The promoting effect of Mg^{2+} ions in electron transfer reduction of substrates may be ascribed to the binding of metal ions to the radical anions being potentially formed in the electron transfer reaction. The increased concentration of superoxide anion radicals due to mediated transfer of electron by Mg^{2+} cations in alkaline medium followed by their increased mobility after water admission may well be responsible for much stronger CL signals

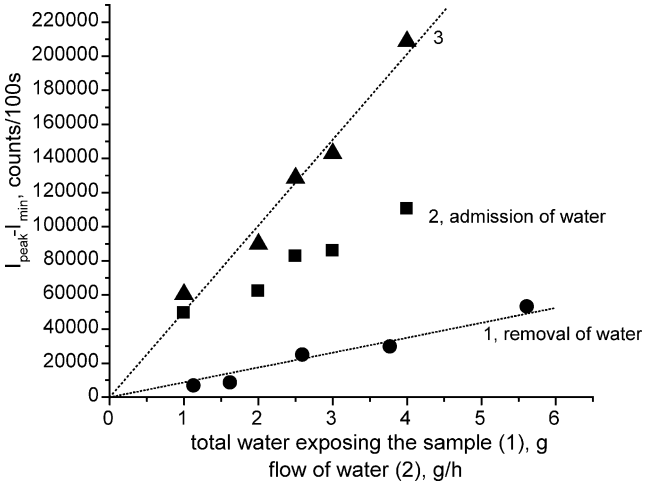


Fig. 9. Correlation between absolute value of chemiluminescence intensity increase after admission (points 2) and removal of water (line 1) on total amount or flow of water exposing Whatman cellulose impregnated with $Mg(HCO_3)_2$, temperature 150 °C, oxygen flow 60 ml/min, straight line 3 is the correction of points (2) to 100% of oxygen.

(Fig. 8) when compared with cellulose non-impregnated by magnesium ions.

Superoxide anion radicals interacting with water give hydrogen peroxyl radicals as follows:

$$O_2^{\bullet} + H_2O \rightarrow {}^{-}OH + HOO^{\bullet}$$

The exothermic source of CL reaction is then expected to be the recombination of hydrogen peroxyl radicals:

$$HOO^{\cdot} + {}^{\cdot}OOH \rightarrow HOOH + O_2^*$$

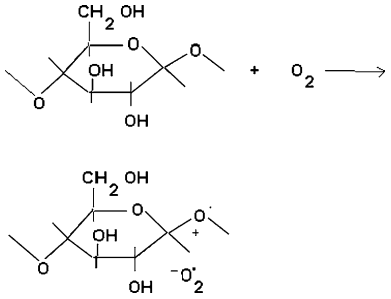
Here O_2^* denotes the singlet oxygen. According to the paper of Reshetnyak, Kovalchuk, Skurski, Rak, and Blazejowski (2003), however, the sequence of subsequent reactions may lead either to ozone and to dimers of singlet oxygen:

$$HOOH + O_2^* \rightarrow O_3 + H_2O$$

$$O_3 + HOOH \rightarrow {}^*(O_2) + H_2O$$

The maximum of emission of one molecule of singlet oxygen is situated at 741 nm while that from emission of singlet oxygen dimers may be found at 460 nm which is identical with maximum spectral sensitivity of photomultiplier used in Lumipol 3 instruments. The above scheme will require the presence of at least one molecule of hydrogen peroxide in the close vicinity of two recombining peroxyl radicals and assumes a large heterogeneity of the oxidation process.

The open question still remains which mechanism leads to the superoxide anion radicals formation. The promoting effect of magnesium cations on CL may be, however, an indication of such initiation step in cellulose oxidation like the direct electron transfer from ether oxygen linking glucopyranosyl units to the molecule of oxygen giving pair of cation radical and superoxide anion radical.



As hydrogen of hydroxyl group at the position 2 is weakly acidic it may be abstracted by superoxide anion-radicals to form hydrogen peroxyl radicals. Simultaneously there may occur the scission of the main chain accompanied by CL by a mechanism which remains to be elucidated.

In the presence of the excess of water, superoxide anion-radicals start to move, the pairs of cation and anion radicals disappear and the relaxation process of CL after water

admission may be due to singlet oxygen emission according to paper Reshetnyak et al. (2003).

4. Conclusions

Addition or removal of water to cellulose paper leads to immediate increase of the light emission which is followed by the relaxation of the signal. It is supposed that removal of water reveals the oxidation sites which become accessible to oxygen while the admission of water enables the better mobility of superoxide anion radicals converting them to hydrogen peroxyl radicals which in recombination may contribute to the observed CL.

The rate constants determined from the CL runs under non-isothermal conditions reflecting the whole oxidation process of cellulose which ultimately leads to main chain scission, temporary crosslinking and/or oxidation of terminal or side chain groups is surprisingly well related with the rate constants determined from polymerization degree measurements. This relation may be found even in the low temperature region.

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