# Degradability of Cellulose Ethers Examined By Nonisothermal Methods

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***Abstract:*** *The degradation of cellulose and its alkyl ethers (methyl and ethyl) in nitrogen and oxygen atmosphere investigated by nonisothermal thermogravimetry and differential scanning calorimetry was compared with hydroxyethyl cellulose and nitrocellulose. Chemiluminescence method has been used in oxygen atmosphere to show on the "preparatory process" of the cellulose derivatives decomposition before the main stream of volatile products is released. From the compensation graph it was found that in nitrogen hydroxyethyl cellulose and nitrocellulose start degradation from the side groups while others by main chain scission. Kinetic parameters of oxidation were evaluated from chemiluminescence runs in oxygen at 200 $^o$C and thermogravimetry runs in oxygen and nitrogen at 300 °C taking into account the formal scheme of 3 parallel first order processes. From these 3 kinetic steps the main degradation process yielding predominating amount of volatile producs was discriminated.*

***Keywords:*** *Nonisothermal thermogravimetry, DSC and chemiluminescence, the rate of heating, cellulose ethers, nitrocellulose*

## I. Introduction

The alkyl ethers of cellulose are largely used as coatings, paintings, additives to food and cosmetics as well as components of composite functional materials [1]. Alkyl structure in the cellulose ether that brings about a relatively good solubility in nonpolar solvents improves the processability when compared with pure cellulose, however, it changes its stability and its resistance towards oxidation. There exists a lot of papers on decomposition of cellulose and its derivatives investigated by nonisothermal thermogravimetry method that are focused on evaluation of kinetic parameters of degradation [2-19]. They obviously describe the procedure leading to the final state of the material when volatile products are released and carbonaceous residue is formed. Such an approach represents a particular part of the formalism used in thermoanalytical chemistry and physics for evaluation of nonisothermal kinetics. In last years very popular became so-called iso-conversional methods that require performing a series of experiments at different linear rates of heating and do not require any "apriori" reaction model. The most used methods are represented by the differential method of Friedman [8] and by the integral methods proposed by Kissinger [9] and Ozawa [10]. These methods are referred as conventional isoconversional methods. More recently, Vyazovkin proposed an advanced non-linear method [14-18]. One can frequently encounter in the literature competitive approach trying to persuade the reader that the set of parameters such as the activation energy and pre-exponential factor that were found by the method used is just the optimal one for the description of the process. One should, however, have in mind that in the case of other nonisothermal methods such as DSC and chemiluminescence that measure the rate of the reaction, isoconversional approach is questionable as we are not able to determine conversion so reliably as it is in nonisothermal thermogravimetry. In the case of nonisothermal thermogravimetry of polymers one should be also aware of the fact that there may exist several intermediate stages from a initial site of degradation to final volatile products that escapes from the reaction pan and the approximation to lower temperatures of the preparatory stage of degradation taking into account the set of above kinetic parameters becomes a pure speculation. The values of activation energy thus become only the number linked to the slope of the nonisothermal thermogravimetry run.

Comparison of nonisothermal DSC runs with those of differential thermogravimetry may throw some more light what is going on at the beginning of the degradation process particularly when we monitor both DSC endo and exotherms that cannot be noticed in differential thermogravimetry runs. However, the approximation of data to conditions corresponding to lower temperatures is risky as well and may involve big errors.

New possibilities of such an extrapolation brings the chemiluminescence method which is considerably more sensitive and allows to obtain the reliable kinetic parameters even at temperatures around 100 $^o$C. The kinetic examination of the degradation by this method has the sense in the presence of oxygen when the intensity of the chemiluminescence signal is strong enough [20-39].

Having this in mind, and taking into the account the papers describing cellulose degradation [40-47], the present paper is focused on comparison of the effect of electropositive alkyl group in methyl, ethyl and hydroxyethyl cellulose ethers on the oxidisability and thermal stability of the cellulose structure. Of interest might be the comparison with the effect of electronegative nitro group in nitrocellulose [2]. The principal methodologies chosen were nonisothermal chemiluminescence in oxygen, thermogravimetry and DSC in both oxygen and nitrogen. A particular approach to the estimation of kinetic parameters involved the application of the formal scheme of three parallel reactions that appears to be ideal when we want to separate the volatilisation of low molar mass additives from those being formed in the degradation process. At the same time the parameters of the most important step of degradation in both the nitrogen and oxygen may thus be easily compared.

## II. Experimental

**Materials**
Cellulose (C) microcrystalline powder, degree of substitution DS=0 was purchased from Fluka Co.
Methyl cellulose (MC) (content of 2% of water). Methyl cellulose is a hydrophilic white powder in pure form and dissolves in cold (but not in hot) water, forming a clear viscous solution or gel. It is sold under a variety of trade names and is used as a thickener and emulsifier in various food and cosmetic products.
Ethyl cellulose (EC) (content of 5% of toluene + ethanol in the ratio 80:20) is mainly used as a thin-film coaterial and in a pure state as an emulsifier in food additives (E462).
Hydroxyethyl cellulose (HEC) (content of 2% of water) is a gelling and thickening agent widely used in cosmetics, cleaning solutions, and other household products.
All the above cellulose ethers were purchased from Tokyo Chemical Industry Co., Ltd.
Nitrocellulose was a white membrane used in biology; it is produced by GE Healthcare (US). The quantitative elemental analysis indicated weight percents of carbon, hydrogen and nitrogen 27.20, 2.93, and 11.76%, respectively.
As it will be seen later all cellulose derivatives (alkyl, nitro ) have degree of substitution DS=2.

**Thermogravimetry**
The change of the sample mass with increasing temperature was measured using a Mettler-Toledo TGA/SDTA 851[e] instrument with the gas (nitrogen, oxygen) flow of 30 ml/min, in the temperature range from room temperature up to 550 °C and various heating rates. Indium and aluminium standards were used for temperature calibration. The initial mass of sample used ranged between 2 and 3 mg, the reproducibility of nonisothermal experiments was bellow 1°C difference at the maximum rate of the release of volatiles; where the variation was higher, the average from 3 repeated runs was chosen.

**Differential scanning calorimetry (DSC)**
Non-isothermal calorimetric curves were obtained using the Mettler-Toledo DSC 821[e] instrument with a nitrogen and oxygen flow of 50 ml/min in the temperature range from 25 to 400°C and three heating rates 2.5°C, 5°C and 10°C min$^{-1}$. Indium was used for calibration of temperature and heat of fusion. The mass of sample varied between 1 and 3 mg.

**Chemiluminescence (CL)**
Chemiluminescence measurements were performed on Lumipol 3 photon-counting instrument manufactured at the Polymer Institute of the Slovak Academy of Sciences (Bratislava, Slovakia). The sample powder was placed on an aluminium pan of diameter 9 mm in the instrument compartment. The oxygen flow through the sample cell was 3.0 L h$^{-1}$. The temperature in the instrument compartment increased linearly with time from 40 °C up to 250 °C, usually at the rate of 5 °C min$^{-1}$. When compared with nonisothermal thermogravimetry and DSC the ramp temperature was only 250 °C as at higher temperatures the light emission from the heating oven might interfere with the signal from the sample oxidation. The signal of the photocathode was recorded at a 10 s data collection interval.

**Principles of chemiluminescence**
Chemiluminscence is an extremely sensitive analytical method with several advantages but also some drawbacks [20,31,32]. It monitors exothermic reactions taking place in a material such as the disproportionation of secondary peroxyl radicals [25] and the termination of alkyl radicals, which form part of more complex degradation processes. These reactions provide the energy for excitation of suitable energy acceptor that must be formed or be present in the reaction system. The energy acceptors are carbonyl groups or singlet molecular oxygen. Relaxation of the excited species results in the emission of the light. Chemiluminescence is thus linked to the rate of formation of initiating sites due to degradative factors such as increased temperature and/or

oxygen. Oxidation usually occurs via hydroperoxide formation, with consumption of oxidisable sites such as $CH_2$, CH, and other carbon containing groups. The gradual consumption of these oxidisable sites may lead to the chain scission or crosslinking. Generally, the more stable polymers have the experimental curve intensity of the light - temperature shifted to a higher temperature.

**The model for evaluation of experimental results from non-isothermal thermogravimetry and chemiluminescence**

The light emission mechanism and formation of volatile products from cellulose heated in a given atmosphere at a certain linear rate of heating is rather complex process that may be more or less successfully described by the formalisms taking into account adequate scheme based on the formal reaction kinetics. In our model we assume that oxidation of the cellulose derivative in oxygen accompanied by the light emission converts it to intermediate products $P_i$ (i=1→3) which subsequently decompose to volatiles $V_{(4→6)}$ leaving a solid residue $T_{(4→6)}$ on the reaction pan (Scheme 1).
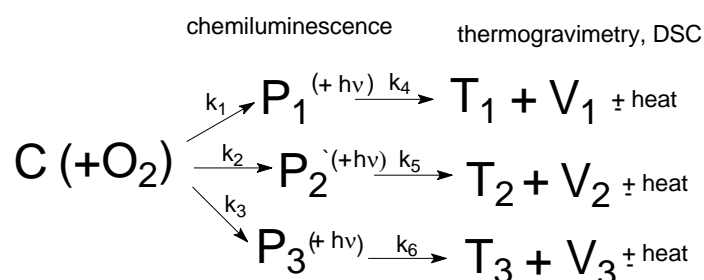


**Scheme 1.** Formalism unifying the light emission (chemiluminescence), heat release (DSC) amd formation of volatiles (thermogravimetry) from the heat and oxygen exposed cellulose ethers.

Oxidation and/or decomposition to volatiles is thus described by a set of parallel reactions where the "preparatory" stage of formation of volatiles is well separated from the higher temperature degradation to volatiles. In this stage, the formation of volatiles is assumed to be negligible. One should be aware that this preparatory stage may well be seen and registered by chemiluminescence in oxygen due to the sequence of oxidation steps demonstrated for methyl cellulose giving rise to alkyl peroxyl radicals A (Scheme 2) that are secondary peroxyl radicals. According to Russel's scheme [25] these radicals in disproportionation provide triplet carbonyl compound (B) alcohol (C) and singlet oxygen (D) (Scheme 3). One should be aware that chemiluminescence monitors the rate of the oxidation process and the calculation of respective parameters should thus be adopted to it.
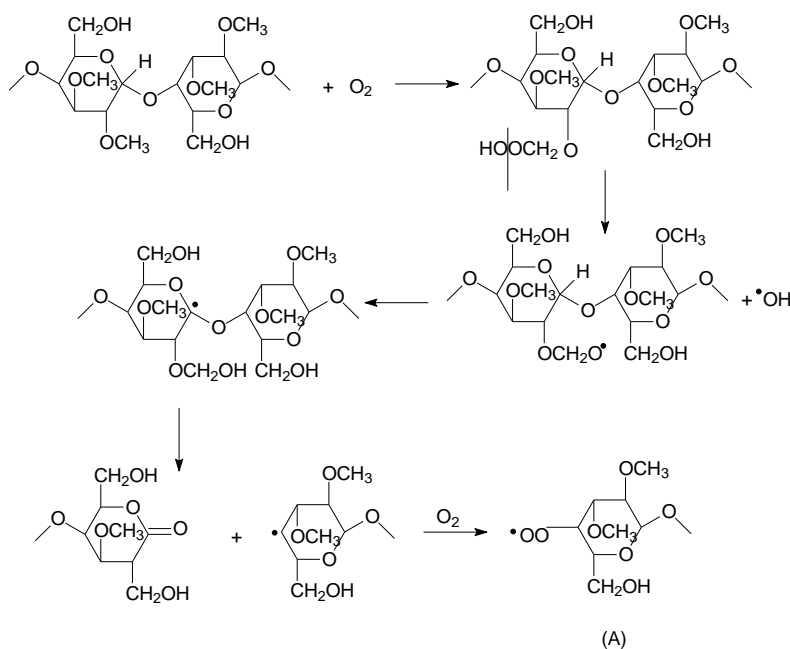


**Scheme 2.** Hydroperoxidation of methyl cellulose and subsequent decomposition of hydroperoxides and the scission of the main chain of cellulose.
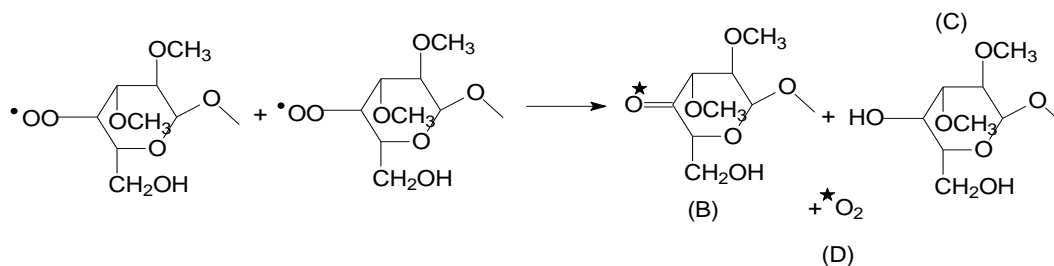
**Scheme 3.** Formation of excited species during the disproportionation of secondary peroxyl radicals in methyl cellulose.

Scheme 2 shows the possible route how the main chain scission may occur. Oxy radicals being formed from hydroperoxide abstract hydrogen in the position 2 of structural glucopyranosyl unit and terminal carbonyl group together with terminal alkyl radicals are formed that subsequently in oxygen provide peroxyl radicals A. In nitrogen, only the steps described by the rate constants $k_{(4 \to 6)}$ can be traced. We are thus facing the formalism of solution of nonisothermal reaction scheme involving several parallel steps. In the case of thermogravimetry and DSC it has been assumed that each step fulfils the scheme of the first order reaction, i.e $-\dfrac{dm}{dt} = km$. In a

non-isothermal mode, $-\dfrac{dm}{dT}\dfrac{dT}{dt} = A \exp\left(-\dfrac{E}{RT}\right)$, where $\beta = \dfrac{dT}{dt}$ is a linear heating rate. After integration,

we obtain

$m = m_0 \exp[-\dfrac{A}{\beta} \int_{T_0}^{T} \exp(-\dfrac{E}{RT})dT]$ , and for the process composed of j (j=4→6) temperature dependent

components - "waves", we have

$$m = m_0 \sum_{i=4}^{6} \alpha_i \exp[-\dfrac{A_i}{\beta} \int_{T_0}^{T} \exp(-\dfrac{E_i}{RT})dT] \qquad 1)$$

Provided that mass changes are expressed as a percentage of the original mass, $m_0$, parameters $\alpha_i, A_i, E_i$ may be found by a nonlinear regression analysis applied to curves of the experimental mass $m$ vs. temperature $T$, from the initial temperature $T_0$ to a final temperature $T$ of the experiment. The rate constant, $k_i$, corresponding to a given temperature is expressed as

$k_i = A_i \exp(-E_i / RT)$ .

The above function 1) was used for fitting of experimental thermogravimetry curves and for evaluation of corresponding pre-exponential factor and activation energy and if necessary the rate constant of the formation of volatiles for the respective fraction of volatiles $\alpha_i$ being formed from the polymer. Here we have focused our attention to the main fraction involving predominating part of the decomposition process.
Chemiluminescence of the degrading material comes from the oxidation of the initial state of the cellulose (the number of parallel steps assumed was j=1→3). The experimental records chemiluminescence intensity vs. temperature provide the rates of the oxidation and should thus correspond to the first derivation of the function 1) as described elsewhere [31].
Picture of DSC appears more complex as it involves the rate of release or absorption of heat in both parts of the right side of the Scheme 1.

## III. Results and Discussion
**Nonisothermal thermogravimetry and differential scanning calorimetry of cellulose ethers**
**Estimation of the degree of substitution of cellulose derivatives**
When applying eq.1 on nonisothermal thermogravimetry runs we obtain kinetic parameters of three parallel processes of the first order including the evaporation of low molar mass solvent, active decomposition into volatiles and carbonization of the degradation residue. Plotting the highest fraction of the conversion of the cellulose derivatives attributed to the active decomposition into degradation products vs. molar mass of glucopyranosyl unit divided by the molar mass of the derivative with the degree of substitution DS=2 we obtain

the linear graph having the slope 1 (Fig.1) confirming that indee, the degree of substitution on cellulose unit wqas 2. This was done for three rates of heating 2.5, 5 and 10 $^{o}$C min$^{-1}$, respectively, and for the experimental records from the Fig. 2.
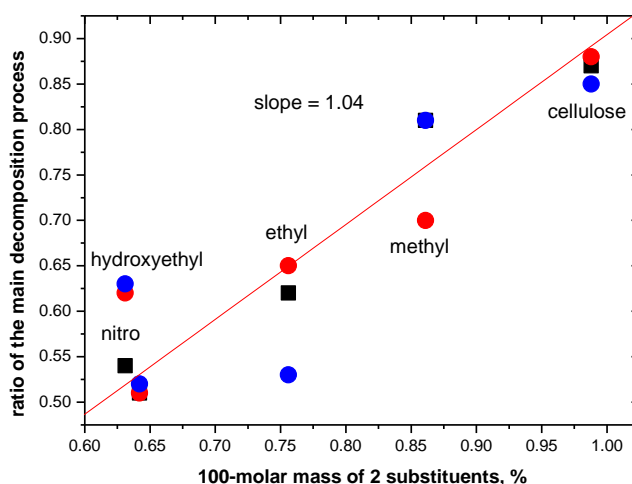


**Fig. 1.** Correlation between the fraction of the main decomposition process and the ratio of the mass of glucopyranosyl unit with that having DS=2
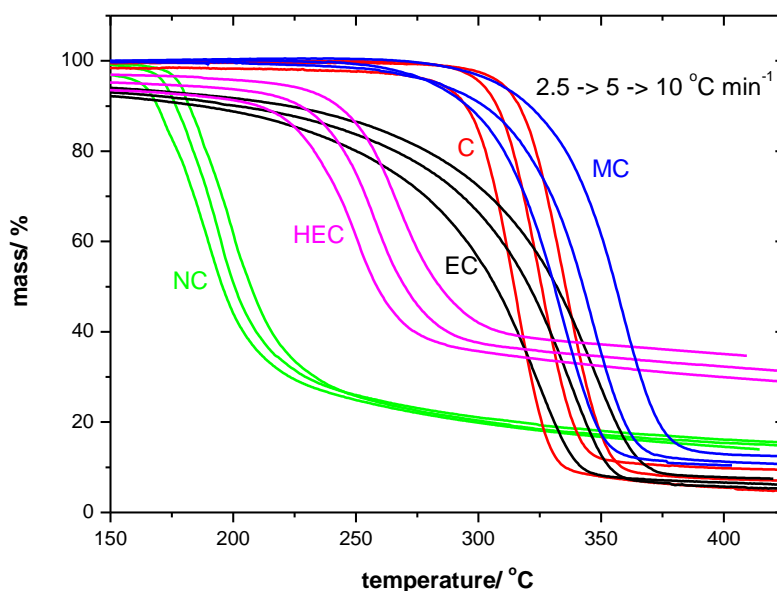


**Fig.2.** Nonisothermal thermogravimetry runs for cellulose (C), methyl cellulose (MC), ethyl cellulose (EC), hydroxyethyl cellulose (HEC) and nitrocellulose (NC) in nitrogen at the rates of heating 2.5, 5 and 10 $^{o}$C min$^{-1}$ (from the left to the right). To receive the better distinction the thermogravimetry runs are presented from temperature 150 $^{o}$C when some low molar mass volatiles were already evaporated.

**Nonisothermal thermogravimetry in nitrogen and in oxygen**

Nonisothermal thermogravimetry runs show on the effect of respective substituents on the thermal stability of cellulose ethers in nitrogen (Fig.2). Active weight loss, i.e. mass loss at the degradation of the sample around the temperature of the maximum rate of release of volatiles for methyl cellulose occurs obviously at highest temperature, however, the slope in maximum of the mass loss is not as steep as that with cellulose. Ethyl cellulose is the third in the sequence of thermal stability, then it is followed by hydroxyethyl cellulose and as expected by nitrocellulose which is the least stable. In the case of ethyl and hydroxyethyl cellulose we have to take into account the evaporation of the solvent present there at lower temperatures and the curve may be somewhat distorted. The increasing rate of heating shifts the temperature of the maximum rate of the mass loss

to higher values. Oxygen accelerates the degradation of cellulose and their derivatives significantly and in comparison with nitrogen shifts the observed experimental curves to lower temperatures (Fig. 3).

Particular behaviour may be seen for hydroxyethyl cellulose and nitrocellulose where the effect of oxygen on nonisothermal DTG runs appears to be less important (Fig. 4). Of interest is that oxygen in nitrocellulose reduces the rate of decomposition when compared to nitrogen.
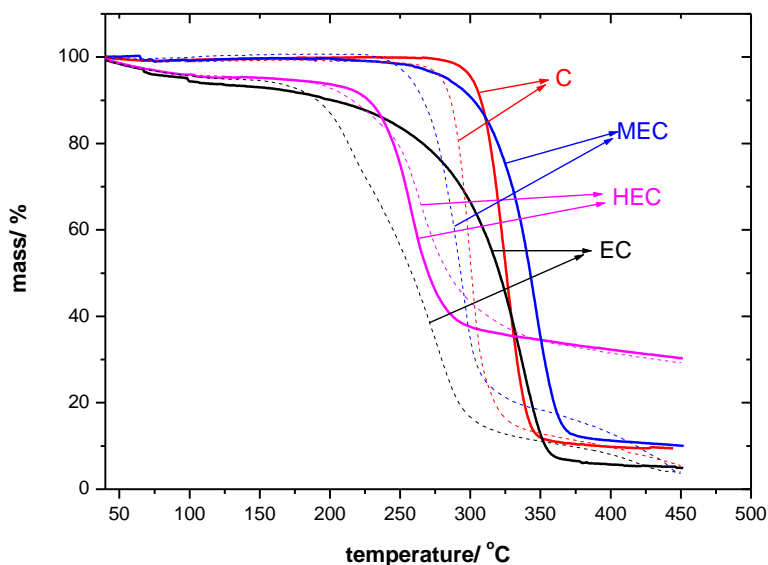


**Fig.3.** Nonisothermal thermogravimetry runs for cellulose (C), methyl cellulose (MC), ethyl cellulose (EC) and hydroxyethyl cellulose (HEC) in nitrogen (full) and in oxygen (dashed) at the rate of heating 5 $^{o}$C min$^{-1}$.
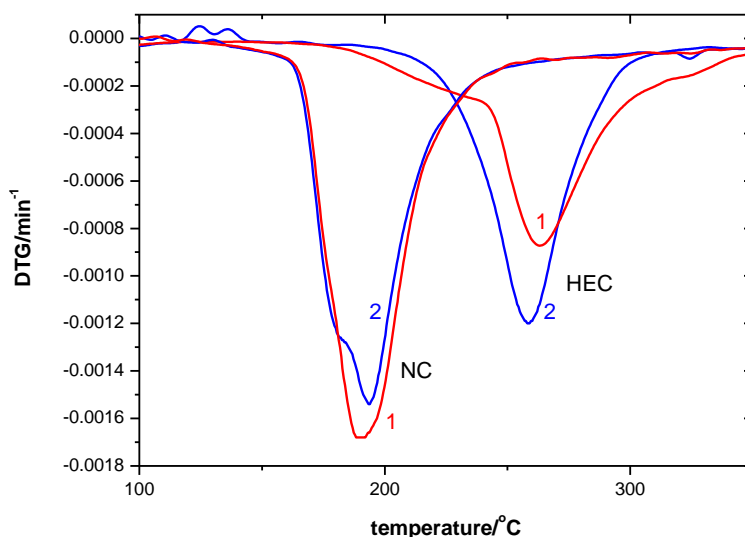


**Fig. 4.** Differential nonisothermal thermogravimetry of hydroxyethyl cellulose (HEC) and nitrocellulose (NC) in nitrogen (1) and in oxygen (2) at the rate of heating 5 $^{o}$C/min.

The rate constants of cellulose ethers (cellulose, methyl cellulose and ethyl cellulose) decomposition in nitrogen determined for the main process and 300 $^{o}$C have the tendency to decay with the increasing rate of heating, no such a tendency was observed for hydroxyethyl cellulose, while for nitrocellulose at 200 $^{o}$C it seems to be quite opposite. In oxygen, the rate constants at 300 of first three ethers are higher than in nitrogen while opposite is true for hydroxyethyl cellulose at 300 $^{o}$C and nitrocellulose at 200 $^{o}$C (Table 1).

The quality of the fitting of experimental thermogravimetry runs for methyl cellulose in nitrogen and oxygen by eq. 1 may be seen in the Fig. 5. Parameters of the main decomposition process are shown in the Table 1.

**Table 1.** Parameters received from the theoretical fits of experimental runs of nonisothermal thermogravimetry (TG) for cellulose (C), methyl cellulose (MC), ethyl cellulose (EC), hydroxyethylcellulose (HEC) and nitrocellulose in nitrogen and oxygen.

| Sample | The rate of heating/ °C min⁻¹ | Fraction of the main decomposition component Nitrogen/oxygen | A/β Nitrogen/oxygen | Activation energy/ kJ mol⁻¹ Nitrogen/oxygen | Rate constant k at 300 °C/s⁻¹ Nitrogen/oxygen |
|---|---|---|---|---|---|
| C | 2.5 | 0.89/0.79 | 1.60e22/1.15e23 | 262.8/261.3 | 1.0e-3/1.1e-2 |
| | 5 | 0.88/0.81 | 5.44e21/3.50e22 | 262.3/260.9 | 8.1e-4/6.9e-3 |
| | 10 | 0.85/0.86 | 1.75e21/1.49e22 | 261.6/261.7 | 6.0e-4/5.0e-3 |
| MC | 2.5 | 0.68/0.83 | 1.10e14/1.27e17 | 177.8/193.2 | 3.5e-4/1.7e-2 |
| | 5 | 0.74/0.74 | 1.16e15/4.90e16 | 193.2/192.8 | 2.3e-4/1.4e-2 |
| | 10 | 0.81/0.66 | 5.12e14/4.74e13 | 192.9/164.8 | 2.2e-4/9.5e-3 |
| EC | 2.5 | 0.62 | 9.6e10 | 139.6 | 9.2e-4 |
| | 5 | 0.65/0.84 | 9.89e10/2.4e4 | 142.9/61.1 | 9.2e-4/5.9e-3 |
| | 10 | 0.53 | 5.3e12 | 165.8 | 8.6e-4 |
| HEC | 2.5 | 0.51 | 2.15e13 | 146.4 | 4.9e-2 |
| | 5 | 0.51/0.51 | 3.1e13/7.0e7 | 153.6/96.6 | 3.2e-2/1.0e-2 |
| | 10 | 0.52 | 3.9e11 | 133.9 | 4.9e-2 |
| | | | | | Rate constant k at 200 °C, s⁻¹Nitrogen/oxygen |
| NC | 2.5 | 0.54 | 1.86e15 | 145.0 | 9.6e-3 |
| | 5 | 0.62/0.74 | 9.1e14/7.10e17 | 144.4/175.4 | 1.1e-2/3.4e-3 |
| | 10 | 0.63 | 1.84e14 | 140.3 | 1.2e-2 |
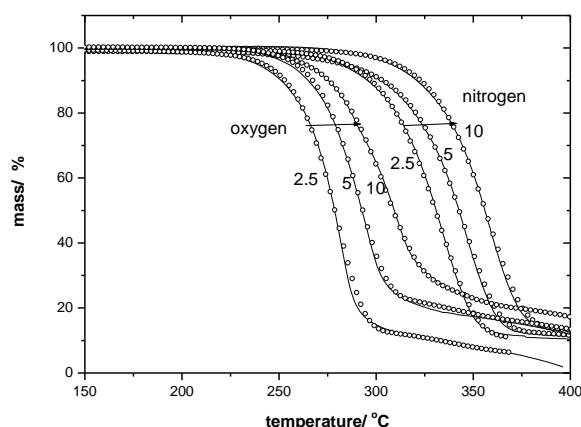


**Fig.5.** Nonisothermal thermogravimetry runs for methyl cellulose in nitrogen and oxygen. The points represent theoretical fit by the eq.1. The numbers denote the rate of heating in °C min⁻¹.
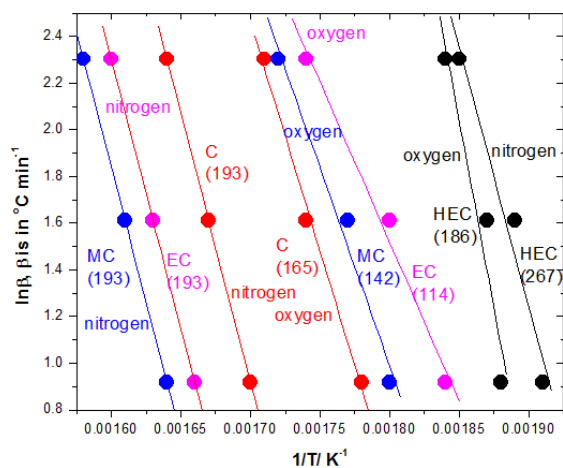


**Fig. 6.** Plots of lnβ vs. 1/$T_{max}$ (β is the rate of heating) for nonisothermal thermogravimetry runs of cellulose (C), methyl cellulose (MC), ethyl cellulose (EC) and hydroxyethyl cellulose (HEC) in nitrogen and oxygen. The graphs were constructed from the data of the temperature of the maximum rate of the release of decomposition products from DTG (Table 2, bold). The numbers denote the temperature coefficient in kJ/mol.

It was of interest to see activation energies that are read from the plot of lnβ vs. 1/T as proposed e.g. by Ozawa [10] (Fig.6). The values for oxygen are lower than those for nitrogen for cellulose and its methyl and ethyl ether while for hydroxyethyl cellulose it is again opposite. These numbers, however, do not have any correspondence with the data in the Table 1 which reflect parameters of the main decomposition process. In this model free process it is thus questionable if the reaction rate can be identified with the rate of heating.

By plotting activation energy E of the main decomposition process against lnA (Fig. 7) for all 3 heating rates in nitrogen we obtain 3 linear compensation graphs. While points for cellulose, methyl and ethyl cellulose may be found on one straight line, those for hydroxyl cellulose and nitrocellulose are separated. This may be explained by the different initial mechanism of degradation. While in the former case the degradation starts by the splitting of C-O-C bridges linking glucopyranosyl units in the latter case it is splitting off the side groups, releasing $HNO_3$ and $H_2O$ from nitrocellulose and hydroxyethyl cellulose, respectively.

**DSC of cellulose derivatives in nitrogen and in oxygen**

In the DSC records we can see typical endothermic peak of pyrolysis for all studied heating rates for cellulose (C) that is probably due to the cleaveage of glycosidic C-O-C bonds [1]. The representative DSC curves of cellulose in nitrogen and oxygen at the three heating rates may be seen in the Fig. 8. It may be of interest that even in oxygen similarly as in nitrogen the experimental runs of DSC records start with endotherms that are shifted to lower temperatures. In oxygen, they are subsequently converted to exotherms. This may be understood so that exotherms correspond to the relatively slow oxidation of methylol groups on glucopyranosyl units that change to carboxyl groups. At the very beginning of the record the latter facilitate the cationic cleavage of C-O-C bridges linking glucopyranosyl units. This cleavage thus appears to be responsible for the endotherms observed before the exotherms of decomposition.

The DSC decomposition curves of methyl cellulose (MC) in nitrogen are characterized by two peaks (Table 2, bold). Their intensity with decreasing heating rate decreases. The first peak is located at the temperature range of cellulose endotherm. Nonisothermal lines for decomposition of methyl cellulose in nitrogen are situated at higher temperatures than those of cellulose. Ethyl cellulose shows different degradation curves for each heating rate. The DSC curve measured with highest heating rate exhibits one peak of pyrolysis, while DSC curve measured at the lowest
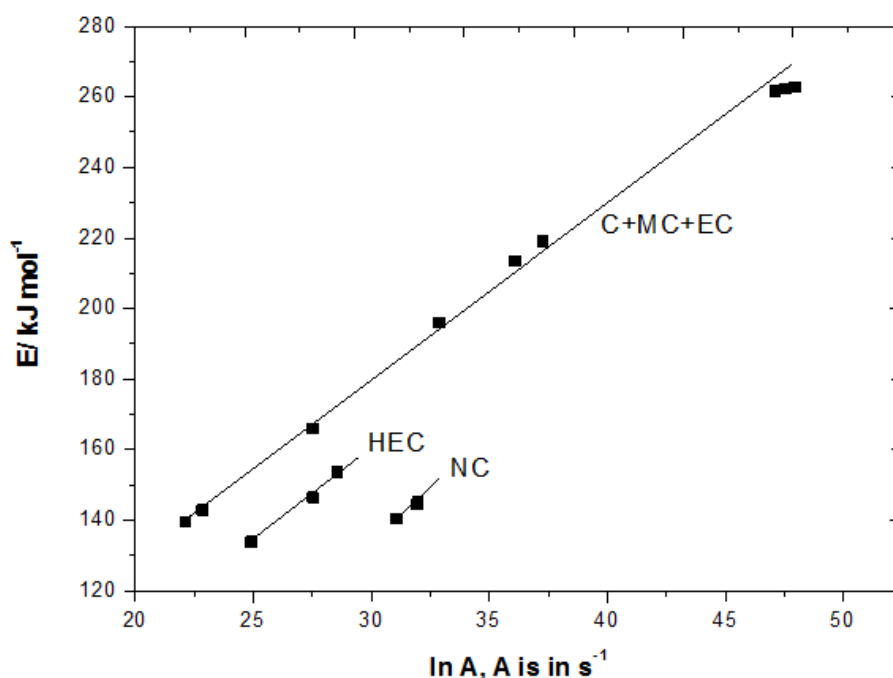


**Fig. 7.** The compensation between activation energy and logarithm of pre-exponential factor for parameters of the predominating decomposition process determined by the theoretical fitting of nonisothermal thermogravimetry experiments in nitrogen at the rates of heating 2.5, 5 and 10 $^{o}$C min$^{-1}$.
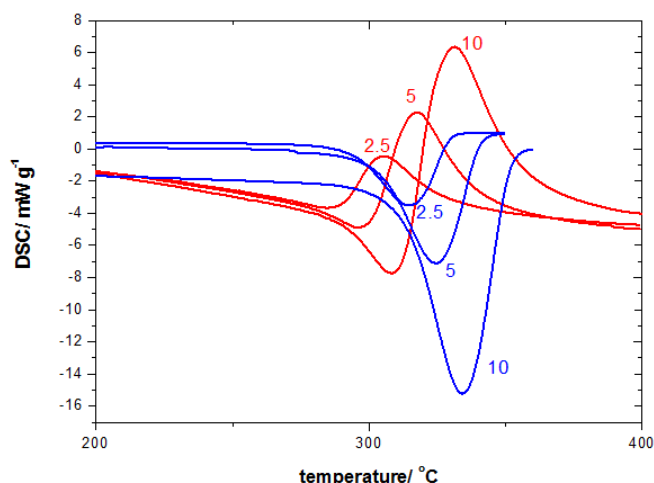
**Fig. 8.** DSC runs for cellulose in oxygen (red) and nitrogen (blue). The numbers are rates of heating in °C min⁻¹

heating rate shows separated two peaks (Table 2, bold). Another character of decomposition is seen for hydroxyethyl cellulose. The presence of hydroxyethyl group in cellulose significantly decreases temperature of degradation. This is due to dehydratation of water from the hydroxyethyl group. Exothermic peak that follows was attributed to the subsequent crosslinking via C=C double bonds. The relatively high carbon residue observed at 400 °C (around 30 % of the mass) corresponds to it (Fig. 2). The values of all thermal characteristics obtained from DSC, TGA and DTG curves for all heating rates are sumarized in the Table 2.

**Table 2.** The values of the DTG and DSC peak temperatures for cellulose, methyl cellulose, ethyl cellulose and hydroxyethyl cellulose at the heating rates 2.5, 5 and 10°C min⁻¹ in nitrogen (bold) and oxygen (several peaks are separated by comma, - no peak)

|  | Cellulose C | Methyl cellulose MC | Ethyl cellulose EC | Hydroxyethyl cellulose, HEC |
|---|---|---|---|---|
| The rate of heating, 2.5 ºC min⁻¹ | Nitrogen/Oxygen | Nitrogen/Oxygen | Nitrogen/Oxygen | Nitrogen/Oxygen |
| Peak DTG/ ºC | **315**/290 | **336**/282 | **328**/269 | **250**/259 |
| Peak DSC/ ºC Endo Exo | **315**/283 <br> **-**/306 | **320,332**/249 <br> -/283 | **329**/- <br> -/151,183,283 | **-**/201,237 <br> **266**/257,320 |
|  |  |  |  |  |
| The rate of heating, 5 ºC min⁻¹ |  |  |  |  |
| Peak DTG/ ºC | **326**/300 | **349**/292 | **341**/281 | **257**/261 |
| Peak DSC/ ºC Endo Exo | **325**/296 <br> -/318 | **326,346**/243 <br> -/298 | **341**/- <br> -/218,290,421 | -/186 <br> **283**/267,327 |
|  |  |  |  |  |
| The rate of heating, 10 ºC /min⁻¹ |  |  |  |  |
| Peak DTG/ ºC | **336**/311 | **361**/309 <br> **342*** | **352**/300 <br> **352*** | **267**/270 <br> **280***/281* |
| Peak DSC/ ºC Endo Exo | **335**/308 <br> -/332 | **330,360**/245 <br> -/293,313 | **350**/- <br> -/217,329,437 | **256**/190 <br> **295**/276 |

*Temperature of the maximum rate of release of volatiles from the paper [1].

DSC records of other derivatives of cellulose are much more complicated (Table 2). E.g. in the case of methyl cellulose in oxygen the shape of the degradation peak is dependent on the heating rate. The double peak character at the highest HR=10°C min⁻¹ is changed to one peak with shoulder (HR=5°C min⁻¹) and to one peak at HR=2.5°C min⁻¹. Ethyl cellulose shows two main peak of degradation at all heating rates. In the case of hydroxyethyl cellulose there obviously occurs dehydratation as the primary step and then two degradation peaks appear at the DSC records, which are more distinct for the lower heating rate. The unsaturated C=C bonds that are formed subsequently crosslink which corresponds to the the second exothermic peak and the carbonisation occurs which may be confirmed by considerably higher carbon residue (Fig. 2).

**Chemiluminescence and TG from cellulose derivatives**

       Typical feature of non-isothermal chemiluminescence runs in oxygen is the sensitivity of the light emission signal to the type of substituents (Fig. 9). Hydroxyethyl and ethyl cellulose give the signal passing through a maximum at 198 and 218 °C, respectively while the light intensity of methyl ether is steadily increasing up to the ramp temperature of 250 °C. The light intensities are much stronger than those for pure cellulose or nitrocellulose. In the case of nitrocellulose the first maximum is situated at 198 °C, the second which corresponds to the oxidation of carbon residue is at 225 °C. Chemiluminescence from oxidized cellulose is steadily increasing up to 250 °C but it is rather low when compared with alkyl ethers. This appears to be an evidence that the luminosity of oxidized cellulose ethers is brought about by the oxidation of alkyl substituents, predominantly. An easier oxidation of hydroxytheyl substituents when compared to ethyl substituents is likely to precede by dehydratation and easier oxidation of unsaturated C=C bonds. The temperature of the maximum mass loss of hydroxyethyl cellulose in oxygen is higher than that of hydroxyethyl cellulose which may indicate again the effect of some crosslinking reaction due to C=C unsaturations in the case of HEC. From thermogravimetry and chemiluminescence runs at 200 °C in oxygen (Table 3) we may see the large discrepancy between the rate constant corresponding to chemiluminescence for pure cellulose and that to thermogravimetry ($1.7\,e-4$ vs. $6.7e-8\ s^{-1}$). This difference is less significant for methyl cellulose ($6e-5$ vs. $6.8e-6\ s^{-1}$), while for ethyl cellulose and hydroxyethyl cellulose it is even less distinct ($6.9e-4$ vs. $3.9e-4\ s^{-1}$ for ethyl cellulose and $7.4e-3$ vs. $1.4e-4\ s^{-1}$ for hydroxyethyl cellulose, respectively). This seems to be an indication that cellulose during the "preparatory" oxidative stage of the loss of the main portion of volatile products changes the structure of methylol group only being oxidized to aldehyde and carboxyl groups while the integrity of the main chain remains preserved. If the hydroxyl hydrogen in this group is replaced by methyl such oxidation takes place with more difficulties. When going to ethyl or hydroxyethyl groups these
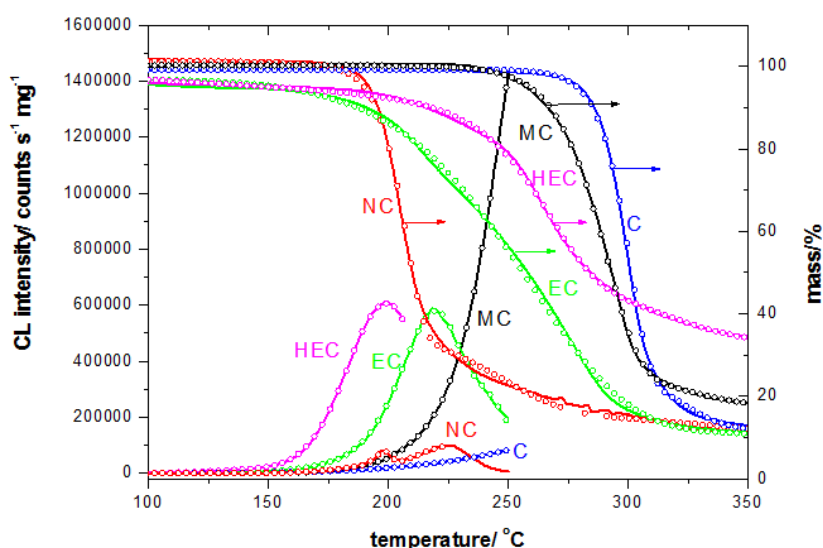


**Fig.9.** Nonisothermal chemiluminescence and thermogravimetry runs for cellulose (C), methyl cellulose (MC), ethyl cellulose (EC), hydroxyethyl cellulose (HEC) and nitrocellulose (NC) in oxygen at the rate of heating 5 °C min$^{-1}$. Points are theoretical fits for 3 process components. The parameters for the main fraction of the process are in the Tables 1 and 3.

are easier to be oxidized when methyls (Table 3). It has also the impact on activation energies determined from chemiluminescence runs that are 87 for cellulose, 169 for methyl cellulose, 126 for ethyl cellulose and 175 for hydroxyethyl cellulose (Numbers are in kJ mol$^{-1}$). This observation supports the assumption shown in the Scheme 2, namely that alkyl substitutents contributes to the main chain scission of cellulose ethers in oxidizing atmosphere and at the same time that one of the two alkyl groups is attached to the methylol units.

**Table 3 .** The rate constants at 200 °C received from the theoretical fits of experimental runs of nonisothermal thermogravimetry (TG) and chemiluminescence (CL) for cellulose (C), methyl cellulose (MC), ethyl cellulose (EC) and hydroxyethylcellulose (HEC) in oxygen for the rate of heating 5°C/min.

| Sample | Fraction of the main decomposition component TG/CL | A/β TG/CL | Activation energy/ kJ mol$^{-1}$ TG/CL | Rate constant k at 200 °C/s$^{-1}$ TG/CL |
|---|---|---|---|---|
| C | 0.81/0.96 | 3.50e22/6.8e6 | 260.9/86.7 | 6.7e-8/1.7e-4 |
| MC | 0.74/0.98 | 4.90e16/2.7e15 | 192.8/169.3 | 6.8e-6/6.0e-5 |
| EC | 0.84/0.56 | 2.4e4/5.8e11 | 61.1/126.2 | 3.9e-4/6.9e-4 |
| HEC | 0.51/0.72 | 7.0e7/1.4e18 | 96.6/175.0 | 1.4e-4/7.4e-3 |

## IV. Conclusions

1.  The decomposition of the cellulose derivatives may start as   a) main chain scission b) reaction on substituents of hydrogen atoms in hydroxyl groups. Both procedures differ in temperatures   of the maximum rate of degradation into volatiles and depend on  atmosphere used, b) being faster than a). In non-substituted cellulose procedure a) predominates. In nonsubstituted cellulose oxygen may initiate the oxidation of methylol groups to carboxyls which may provoke the main chain cleavage by cationic mechanism. Alkyl substitution of this groups contributes to the main chain scission.

2.  While for other cellulose ethers investigated oxygen has significant effect on the reduction of the temperature of degradation in maximum rate, in nitrocellulose and hydroxyethyl cellulose oxygen has almost no effect.

3.  From the compensation graphs for cellulose, methyl cellulose and ethyl cellulose compared with those for hydroxyethyl cellulose and nitrocellulose one may also deduce  that the  decomposition process starts as the main chain scission for the former compounds while scission and following transformation of the side groups in the case of latter.

4.  With the increasing rate of heating the rate constants determined for the main decomposition process for cellulose, methyl cellulose and ethyl cellulose at 300 °C are lower.

5.  Carbon atoms containing substituents increase the intensity of the light emitted (chemiluminescence) during the oxidation of cellulose ethers significantly.

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