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PREDICTION OF THERMAL STABILITY OF FRESH AND AGED PARCHMENT

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The hyphenated thermal analysis-mass spectrometry technique (TA-MS) was applied for the investigation of the thermal behavior of reference and aged parchment samples. The kinetic parameters of the process were calculated independently from all recorded TA and MS signals. The kinetic analysis showed the distinct dependence of the activation energy on the reaction progress. Such behavior is characteristic for the multistage mechanism of the reaction.

The comparison of the kinetic parameters calculated from the different signals i.e. TG, DSC, MS for H_2O, NO and CO_2, however, indicated that they were differently dependent on the aging of the sample. For the parchment samples, the aging almost does not change the kinetics of the decomposition calculated from the DSC data: the influence of aging seems to be too negligible to be detected by these techniques. On the other hand, the much more sensitive mass spectrometric technique applied to the kinetic analysis allowed monitoring of visible changes in the thermal behavior of the parchment samples due to the aging process. The influence of aging was especially visible when the MS signals of water and nitric oxide were applied for the determination of the kinetic parameters.

The applied method of the kinetic analysis allowed also the prediction of the thermal behaviour of reference and aged parchment samples under isothermal and modulated temperature conditions. Presented results have confirmed the usefulness of thermoanalytical methods for investigating behaviour of such complicated systems as leather or parchment.

Keywords: *cultural heritage, hyphenated thermal analysis-mass spectrometry, kinetics, parchment, TG-MS, thermal ageing*

Introduction

Generally kinetic analysis of decomposition processes can be applied to any type of thermoanalytical data (DSC, DTA, TG, TG-MS or TG-FTIR) for the study of raw materials and products within the scope of research, development and quality assurance. The method begins with the determination of the kinetic parameters for a given substance used later to predict the reaction progress under various temperature ranges and conditions when the direct investigation of the reactions is very difficult as e.g. at low temperatures (requiring very long times), as well as under complex temperature profiles. The rate and the progress of the reactions can be predicted for different temperature profiles such as: isothermal, non-isothermal, stepwise, modulated temperature or periodic temperature variations, rapid temperature increase (temperature shock), real atmospheric temperature profiles (up to 7000 places in the world) and even for adiabatic conditions [1].

Process analysis and application

In this study which was performed in the framework of the EC-funded project ‘Improved Damage Assessment of Parchment’ IDAP EVK4-CT-2001-00061 we report on a new application of this approach to investigate the thermal stability of unaged and aged parchment [2]. In order to check the influence of ageing on the thermal stability, the kinetic parameters of the decomposition/oxidation processes were calculated from TA and MS signals recorded at different heating rates. In order to correctly apply the MS signals for the description of the kinetics of the decomposition, the time lag between the thermoanalytical curves (e.g. TG) and MS signal has to be negligible. If this condition is fulfilled, the mass spectrometric signal can be used not only for the qualitative and quantitative analysis of the gaseous products but also for the kinetic description of the process as well [3].

The thermal degradation of the parchment samples was carried out in the atmosphere of 20 vol.% O_2/Ar, the gaseous products of decomposition and/or oxidation: water, nitric oxide and carbon dioxide (m/z=18, 30 and 44) were monitored by MS. Using experimental DSC and TG-MS measurements were performed on the examined samples, the kinetic characteristics of the reaction were determined. The calculated kinetic parameters were subsequently employed to predict the reaction progress of the investigated samples under any given temperature mode.

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Determination of the kinetic characteristics

Theory

The noticeable weakness of the ‘single curve’ methods (determination of the kinetic parameters from single run recorded with one heating rate only) has led to the introduction of ‘multi-curve’ methods over the past few years, as discussed in the International ICTAC Kinetics project [4–7]. Only series of non-isothermal measurements carried out at different heating rates can give a data set, which generally contains the necessary amount of information required for full identification of the complexity of a process [8, 9]. This data set usually contains:

- the relationship between specific conversion α_i and temperatures for different heating rates (non-isothermal mode)
- the relationship between specific conversion α_i and time for different temperatures (isothermal mode)

With $B(T)$ the baseline, $S(T)$ the differential signal, the reaction progress $\alpha(T)$ can be expressed as

$$\alpha(T)=\frac{\int_{T_0}^{T}[S(T)-B(T)]\mathrm{d}T}{\int_{T_0}^{T_{end}}[S(T)-B(T)]\mathrm{d}T} \qquad (1)$$

The tangential area-proportional baseline is the most widely applied because of its correction possibilities [10]. It is created at $\alpha(T)\Rightarrow 0$ and at $\alpha(T)\Rightarrow 1$ by the appropriate tangents at the beginning or the end of the measured signals. This type of baselines can be described by the following equation:

$$B(T)=(1-\alpha(T))(a_0+b_0T)+\alpha(T)(a_1+b_1T) \qquad (2)$$

with (a_0+b_0T): tangent at the beginning of the signal $S(T)$, (a_1+b_1T): tangent at the end of the signal $S(T)$.

$B(T)$ can be calculated iteratively. The convergence is achieved as soon as the relative average deviations between two iterations are smaller than an arbitrarily chosen value (for example 1e-6). The construction of all baselines has to be performed successively for all curves obtained with different heating rates. The normalization of the thermoanalytical signals can then be obtained after baseline subtraction by using the following transformation:

$$S(T)_{\mathrm{normed}}=\frac{S(T)}{\int_{T_0}^{T_{end}}[S(T)-B(T)]\mathrm{d}T} \qquad (3)$$

The isoconversional methods extensively studied by Friedman [11] and Ozawa–Flynn–Wall [12, 13] were applied in the present study. A detailed analysis of the various isoconversional methods (i.e. the isoconversional differential and integral methods) for the determination of the activation energy has been reported by Budrugeac [14]. The convergence of the activation energy values obtained by means of a differential method (Friedman) with those resulted from using integral methods with integration over small ranges of reaction progress α comes from the fundamentals of the differential and integral calculus. Friedman analysis, based on the Arrhenius equation, applies the logarithm of the conversion rate $\mathrm{d}\alpha/\mathrm{d}t$ as a function of the reciprocal temperature at different degrees of the conversion. As $f(\alpha)$ is constant at each conversion degree α_i, the method is so-called ‘isoconversional’ and the dependence of the logarithm of the reaction rate over $1/T$ is linear with the slope of $m=E/R$ as presented in Fig. 1. Decomposition reactions are often too complex to be described in terms of a single pair of Arrhenius parameters and the commonly applied set of reaction models. As a general rule, these reactions demonstrate profoundly multi-step characteristics. They can involve several processes with different activation energies and mechanisms. In such situation the reaction rate can be described only by complex equations, where the activation energy term is no more constant but is dependent on the reaction progress α ($E\neq$const but $E=E(\alpha)$) (Fig. 1) [8, 9, 11–14].

As far as isoconversional integral methods are concerned, these techniques are based on the equation:

$$g(\alpha)=\int_0^{\alpha}\frac{\mathrm{d}\alpha}{f(\alpha)}=\frac{A}{\beta}\int_{T_{\alpha=0}}^{T}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T \qquad (4)$$

where $g(\alpha)$ is the integral conversion function and the $f(\alpha)$ function dependent on the reaction model. The isoconversional integral methods with the integration over low ranges of the degree of conversion and respectively temperature, are based on the equation:

$$g(\alpha-\Delta\alpha,\alpha)=\int_{\alpha-\Delta\alpha}^{\alpha}\frac{\mathrm{d}\alpha}{f(\alpha)}=\frac{A}{\beta}\int_{T_{\alpha-\Delta\alpha}}^{T_\alpha}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T \qquad (5)$$

which is derived by supposing that in the range of the variation of the conversion degree $\Delta\alpha$, the activation energy E can be assumed constant. Obviously, the use of such an approach leads to a plot of E *vs.* the degree of conversion α. However, the activation energy as a function of the conversion progress looks like a stair function in which the low ranges of $\Delta\alpha$ where E keeps a constant value are clearly marked. The number of stairs depends directly on the size of $\Delta\alpha$. In order to evaluate the integrals from the previous equation, one can use the theorem of the average value, we obtain:

$$\frac{1}{f(\alpha_{\xi})}\Delta\alpha = \frac{A}{\beta}\exp\left(-\frac{E}{RT_{\xi}}\right)\Delta T \qquad (6)$$

where $(\alpha-\Delta\alpha)<\alpha_{\zeta}<\alpha$, $T_{\alpha-\Delta\alpha}<T_{\xi}<T_{\alpha}$ and $\Delta T=T_{\alpha}-T_{\alpha-\Delta\alpha}$.

Since the number of stairs (where the activation energy E is assumed constant in the isoconversional integral methods) depends directly on the range of chosen $\Delta\alpha$, an unlimited number of stairs can be reached by making $\Delta\alpha$ infinitesimal for calculating the dependence of the activation energy $E(\alpha)$ at each conversion degree α. For $\Delta\alpha\Rightarrow 0$, we have $T_{\xi}\Rightarrow T$ and $f(\alpha_{\xi})\Rightarrow f(\alpha)$. A consequence is that the previous equation turns back into its differential form:

$$\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T} = A\exp\left(-\frac{E}{RT}\right)f(\alpha) \qquad (7)$$

that grounds the isoconversional differential methods, which corresponds to the Friedman approach applied in the present study. More generally, the conversion rate expression can be adapted to an arbitrary variation of temperature (as well as to isothermal conditions) by replacing ($\beta\mathrm{d}\alpha/\mathrm{d}T$) with $\mathrm{d}\alpha/\mathrm{d}t$.

Friedman analysis applies the logarithm of the Arrhenius equation. The function dependent on the reaction model $f(\alpha)$ becomes a constant at each conversion degree $\alpha_{i,j}$ (‘isoconversional method’) and the dependence of the logarithm of the reaction rate over $1/T$ is linear with the slope of E_i/R (with i: index of conversion, j: index of heating rate). The activation energy as a function of the reaction progress for decomposition of the examined samples can thus be calculated by applying the following equation:

$$\ln\frac{\mathrm{d}\alpha}{\mathrm{d}t}\bigg|_{\alpha_i} = \ln(A_i f(\alpha_{i,j})) - \frac{E_i}{RT_{i,j}} \qquad (8)$$

with i – index of conversion, j – index of the curve and $f(\alpha_{i,j})$ the function dependent on the reaction model that is constant for a given reaction progress $\alpha_{i,j}$ for all curves j.

The linear dependence of the logarithm of the reaction rate over $1/T$ with the slope of E/R for the different conversion degrees α_i allows the determination of the activation energy on the reaction progress, $E(\alpha)$, by making $\Delta\alpha$ infinitesimal. It is displayed in the range of 1 up to 99% in Fig. 1 with the experimental data. As illustrated in Fig. 1, the various reaction courses cannot be described by a single mechanism because the resulting activation energy (Fig. 2) is not constant but is a function of the reaction progress. It shows that the decomposition of the examined substances follows complex reactions which cannot be described in terms of a single pair of Arrhenius parameters.

The accurate determination of the kinetic parameters under experimental conditions applied, which

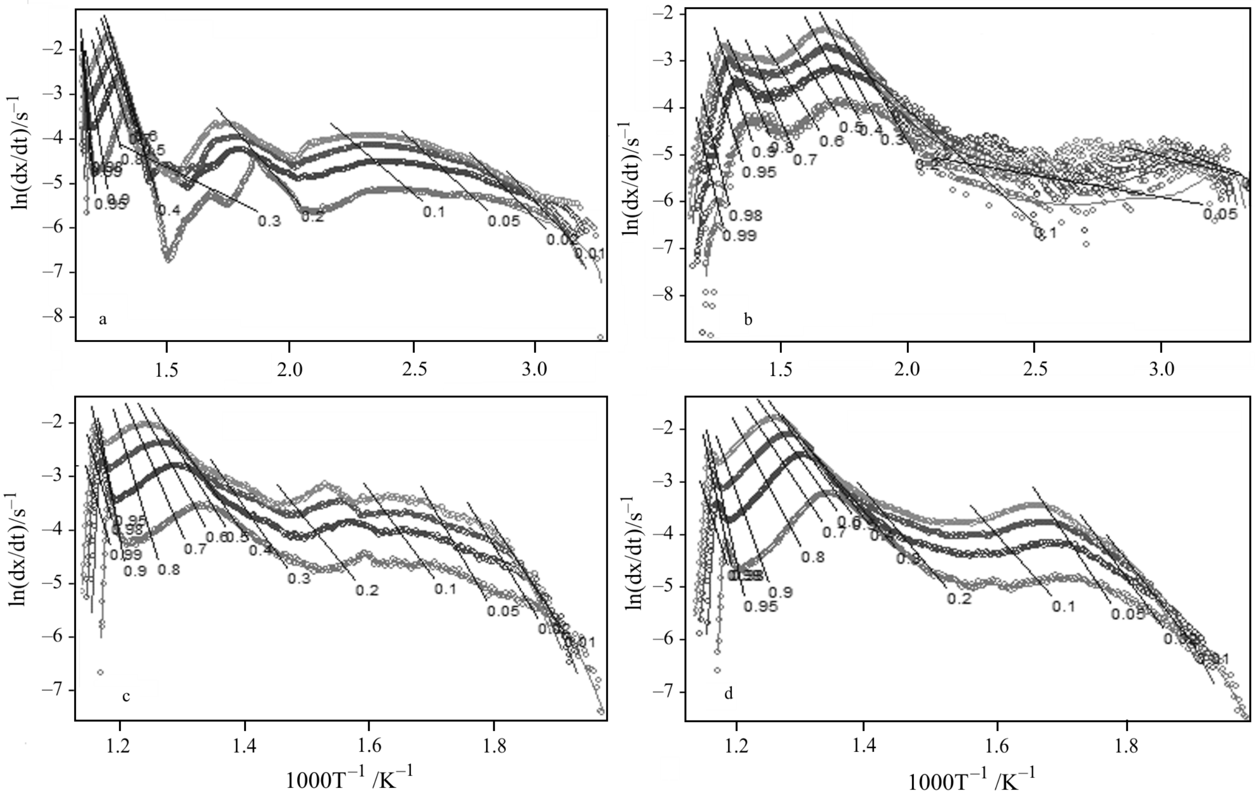

Fig. 1 Friedman analysis for the decomposition of the aged parchment samples: a – DSC, b – MS (m/z=18), c – MS (m/z=30) and d – MS (m/z=44)

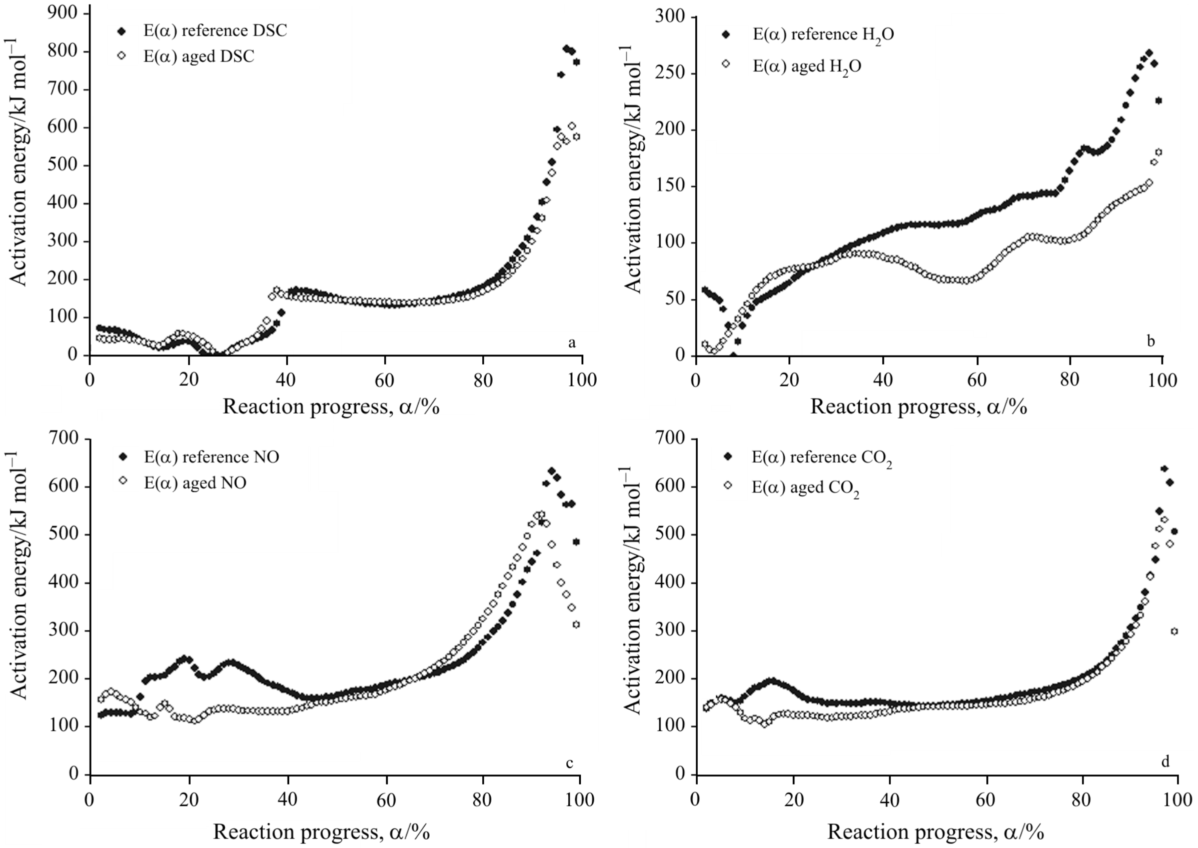

Fig. 2 Activation energy (determined by Friedman analysis after baseline optimization) as a function of the reaction progress α for the decomposition of the reference and aged parchment samples: a – DSC, b – MS (m/z=18), c – MS (m/z=30) and d – MS (m/z=44)

enables the correct fit of the experimental data, is a prerequisite for prediction of the reaction progress under any new temperature profile. However, it is important to note that the baseline construction, especially in the case of investigations by DSC or DTA methods, can significantly influence the determination of the kinetic parameters of the reaction. Therefore, when solving the complicated interrelation between the baseline, the kinetic parameters of the reaction and reaction progress, other considerations can be made besides the isoconversional approach to improve the determination of the kinetic parameters. Moreover, the correct baseline determination should be intimately combined with the computation of the kinetic parameters for the investigated reaction.

When measuring the progress of a reaction one tries to eliminate the systematic errors, so that only accidental errors have to be taken into account. The measured values will spread around the average value for each heating rate. It can be assumed that such distributions have a form of a Gaussian-type curve. The Gaussian distribution results from a summation of several events e.g. overlapping reactions, noise, drift, artefact, uncertainties in the baseline construction, etc.

Therefore, during the optimization, the true information has to be extracted by fulfilling the isoconversional principle and the assumed Gaussian-type distributed errors. These conditions enable to find out for each heating rate the ‘best value’ or ‘central tendency’ of the thermoanalytical signal, for which the chance of the good reproducibility on subsequent measurements is maximal. This makes possible the iterative calculation and objective determination of the correct baseline for each signal measured under different heating rates. This objective determination under respect of the isoconversional assumption is carried out by the optimization of all tangent parameters a_0, b_0, a_1, b_1 for each heating rate β with:

- a_0, b_0=parameters of the slope and intercept of the tangent at the beginning of the signal $S(T)$ with the heating rate ‘β’.
- a_1, b_1=parameters of the slope and intercept of the tangent at the end of the signal $S(T)$ with the heating rate ‘β’.

The baselines are no more only arbitrarily chosen by the users but objectively optimized with:

- statistics, for the consideration of the experimental noise and shape of the signals,
- the isoconversional principle, for the consideration of reaction rates following Arrhenius relationship.

Results and discussion

Comparison of the experimental and predicted course of the DSC and MS signals

The data collected during non-isothermal experiments carried out with different heating rates were used for the determination of the kinetic parameters used later for the prediction of the reaction progress (Figs 3–6).

The comparison of the kinetic parameters calculated from the different signals i.e. DSC, MS for H_2O, NO and CO_2 indicates that they are differently dependent on the sample's aging. This influence can be reported approximately by calculating the average deviation of all activation energies at each conversion degree α:

$$\frac{1}{n}\sum_{i=1}^{n}\mathrm{abs}(E(\alpha_i)_{\mathrm{aged}}-E(\alpha_i)_{\mathrm{reference}}) \quad \text{for } i=1 \text{ to } n=99 \tag{9}$$

from 1% to 99% reaction progress α (Table 1).

The highest mean deviation of the activation energy denotes the thermoanalytical signals where the aging has the largest influence on the thermal stability.

Once the kinetic parameters are determined, they can be applied to compare and predict the evolution of all signals during the substance decomposition under different temperature modes. The influence of the aging can be easily observed when predicting the reaction progress under e.g. isothermal conditions. The ag-

Table 1 Comparison of the mean activation energy deviation over the whole range of reaction progress α for the reference and aged parchment samples

	DSC	m/z=18	m/z=30	m/z=44
Mean activation energy deviation/kJ $\mathrm{mol^{-1}}$	22.9	38.3	54.2	23.7

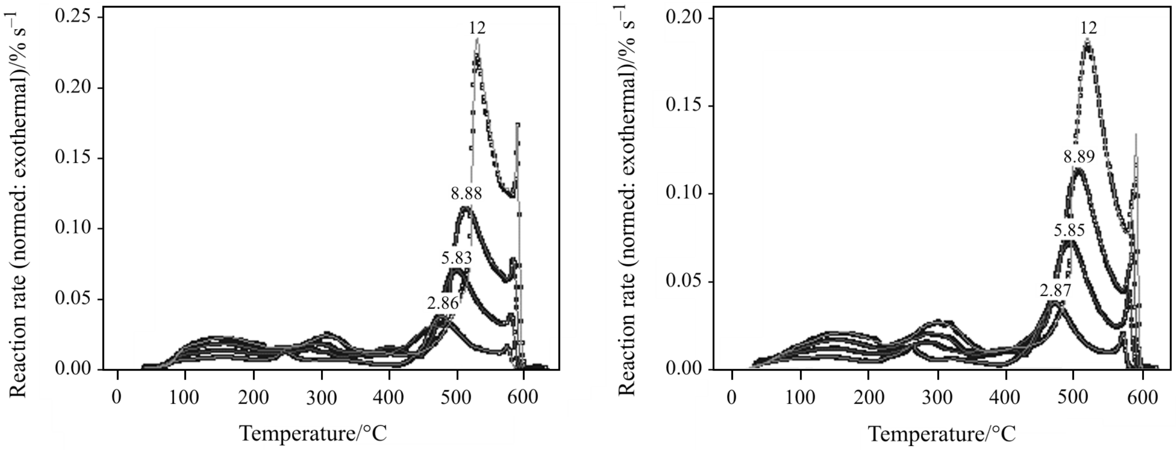

Fig. 3a Normalized DSC-signals as a function of the temperature for parchment samples (left – reference, right – aged). Experimental data are represented as symbols, solid lines represent the calculated signals. The values of the heating rate in °C $\mathrm{min^{-1}}$ are marked on the curves

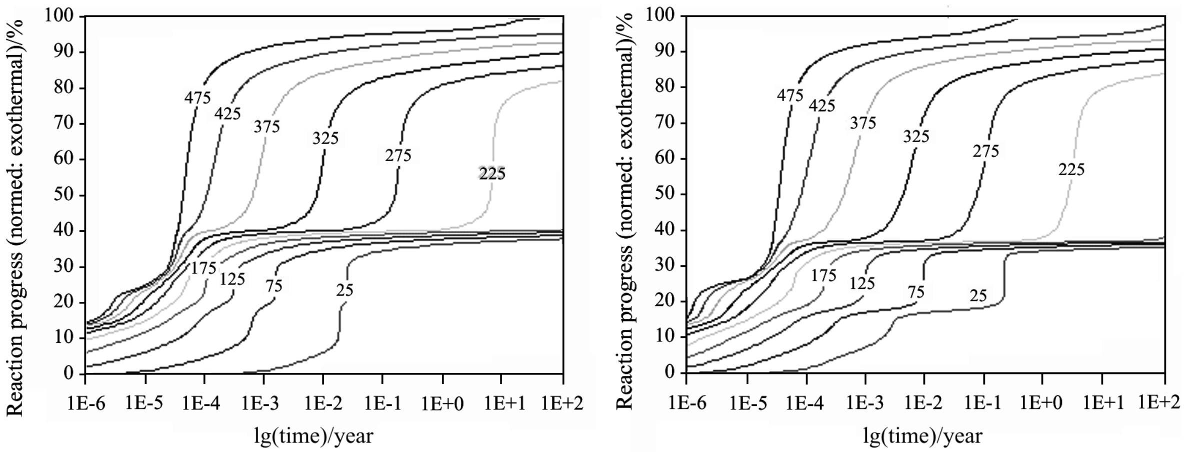

Fig. 3b Calculated reaction progress α (normalized DSC signals expressed as reaction progress) of parchment as a function of time under isothermal conditions (left – reference, right – aged). The values of the temperature in °C are marked on the curves

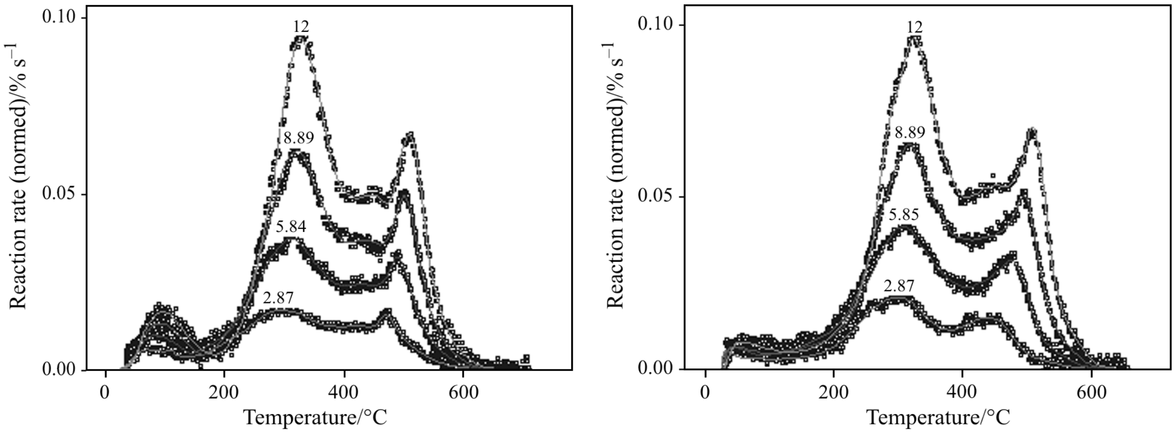

Fig. 4a MS signals (H_2O evolution, normalized signals) recorded during thermal degradation of parchment as a function of the temperature for 4 different heating rates. Experimental data are represented as symbols, solid lines represent the calculated signals. The values of the heating rate in °C min^{-1} are marked on the curves; (left – reference, right – aged)

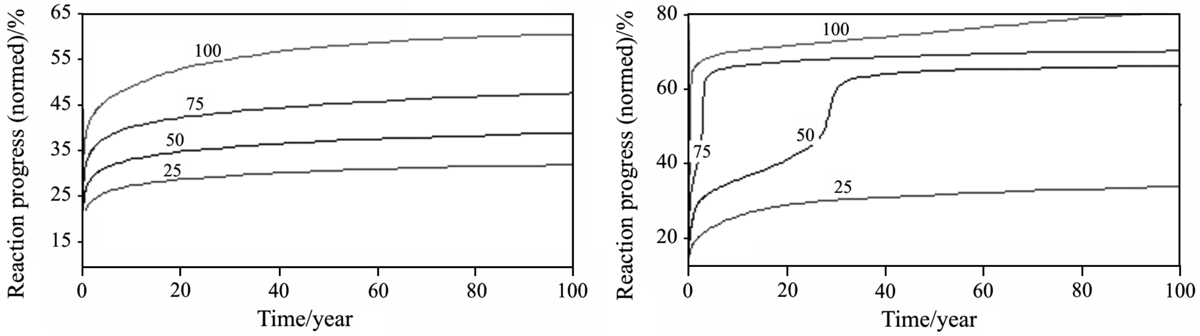

Fig. 4b H_2O evolution (normalized MS signals expressed as reaction progress) during the decomposition of parchment under isothermal conditions (left – reference, right – aged). The values of the temperature in °C are marked on the curves

ing almost does not change the kinetics of the decomposition calculated from the DSC signals (Figs 3a, b). The influence of aging seems to be too negligible to be detected by this technique. However, much more sensitive spectrometric technique applied for the kinetic analysis allowed monitoring visible changes of the thermal behavior of the parchment samples due to the aging process. The influence of aging was especially visible when the MS signals of water (Figs 4a, b) and nitric oxide (Figs 5a, b) were applied for the determination of the kinetic parameters.

Under isothermal conditions the maximal rate of decomposition occurs at the beginning of the reaction. The reaction progress extends thereafter over years,

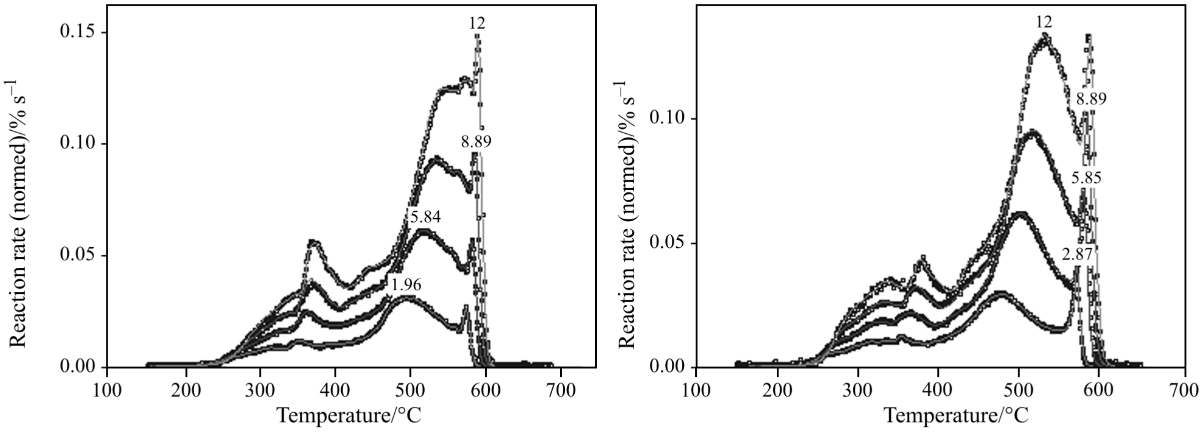

Fig. 5a MS signals (NO evolution, normalized signals) recorded during thermal degradation of parchment as a function of the temperature for 4 different heating rates. Experimental data are represented as symbols, solid lines represent the calculated signals. The values of the heating rate in °C min^{-1} are marked on the curves (left – reference, right – aged)

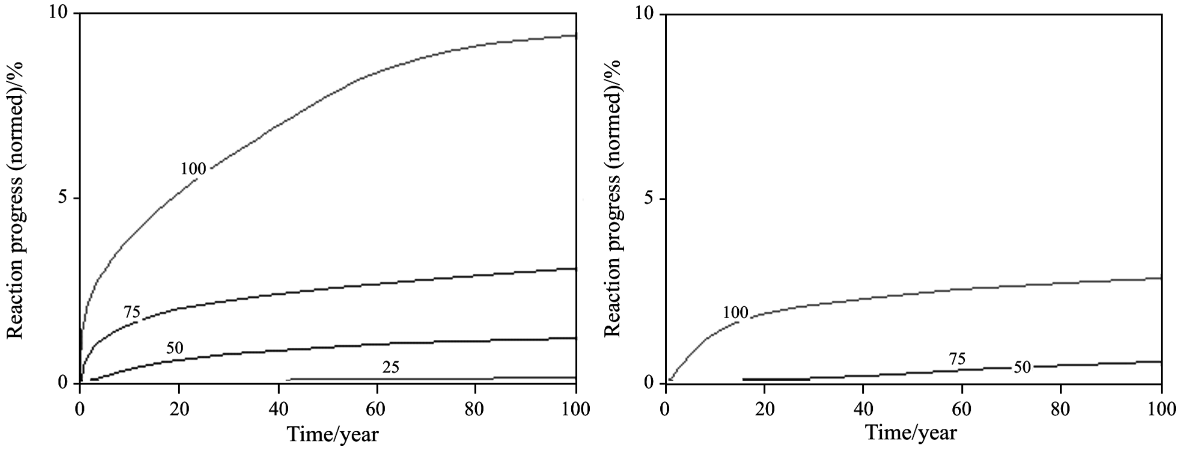

Fig. 5b NO evolution (normalized MS signals expressed as reaction progress) during the decomposition of parchment under isothermal conditions (left – reference, right – aged). The values of the temperature in °C are marked on the curves

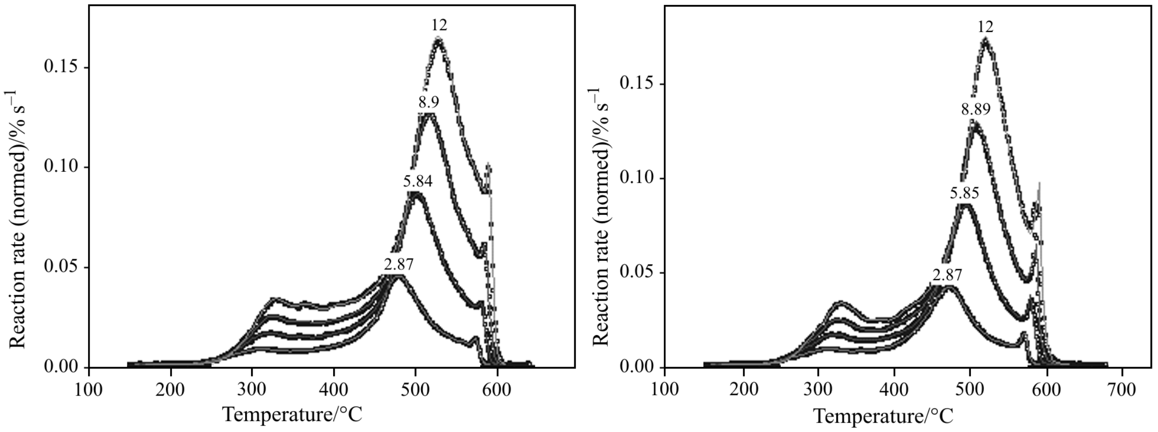

Fig. 6a MS signals (CO_2 evolution, normalized signals) recorded during thermal degradation of parchment as a function of the temperature for 4 different heating rates. Experimental data are represented as symbols, solid lines represent the calculated signals. The values of the heating rate in °C min^{-1} are marked on the curves (left – reference, right – aged)

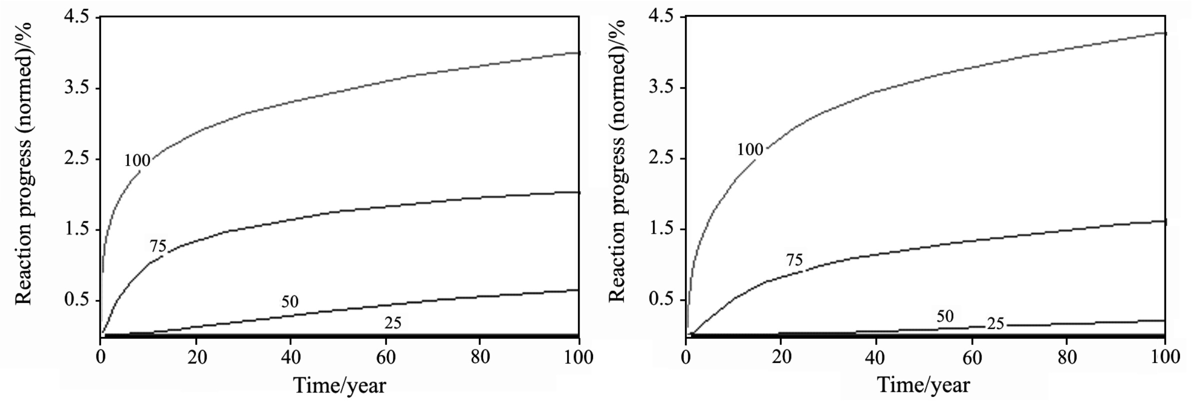

Fig. 6b CO_2 evolution (normalized MS signals expressed as reaction progress) during the decomposition of parchment under isothermal conditions (left – reference, right – aged). The values of the temperature in °C are marked on the curves

which clearly indicates the limitations of experimental applications for isothermal conditions for the examined reaction. The non-isothermal experiments and the determination of the thermokinetics, suppress the time restriction problem and consequently the limitations of measuring the reaction progress under isothermal conditions. If the kinetic data gathered from the non-isothermal data are able to correctly describe the full temperature range, then they can be employed for the prediction of the isothermal reaction progress occurring at temperatures lying inside the range of the non-isothermal experiments such as e.g. during the isothermal conditions. This is especially of interest for multi-step processes where several volatile species are evolved. For such processes, the accurate mathematical transformation of non-isothermal data to isothermal data is straightforward, whereas the inverse procedure is impossible for timing reasons.

Conclusions

The study focused on prediction of the behavior of parchment samples for obtaining a deeper insight into the reaction course of reference and aged parchment samples. The kinetic analysis were done on the basis of TA-MS experiments carried out with different heating rates, generally in the range of 1 to 15 K min^{-1}. The significant difference in the course of the evolution of H_2O between reference and aged samples, and, in turn, in the kinetic parameters of this reaction, indicates the influence that conditioning at higher RH has had on the properties of the parchment. Further studies will be made at different values of RH and applying the several cycles of RH ageing. The additional difference in the rate of evolution of NO between the reference and aged samples indicates that the conditioning at higher RH retarded the progress of this reaction and affected the thermal stability of the collagen polymer network. This is in accord with other observations made by dynamic mechanical thermal analysis which have been reported elsewhere (http://www.idap-parchment.dk).

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