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Application of model-free and multivariate non-linear regression methods for evaluation of the thermo-oxidative endurance of a recent manufactured parchment

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Abstract The thermo-oxidative degradation of a parchment recent manufactured from a goat skin has been investigated by TG/DTG, DSC simultaneous analysis performed in static air atmosphere, at six heating rates in the range 3–15 K min^{-1}. At the progressive heating in air atmosphere, the investigated material exhibits three main successive processes occurring with formation of volatile products, namely the dehydration followed by two thermo-oxidative processes. The processing of the non-isothermal data corresponding to the first process of thermo-oxidation was performed by using Netzsch Thermokinetics—a Software Module for Kinetic Analysis. The dependence of activation energy, evaluated by isoconversional methods suggested by Friedman, and Ozawa, Flynn and Wall, on the conversion degree and the relative high standard deviations of this quantity show that the investigated process is a complex one. The mechanism and the corresponding kinetic parameters were determined by Multivariate Non-linear Regression program. Three mechanisms, one consisting in four successive steps and two others in five successive steps, exhibit the best F-test Fit Quality for TG curves. It was also used the previously suggested criterion, according to which the most probable process mechanism correspond to the best agreement between $E_{FR} = E_{FR}$ (α) (E_{FR} is the activation energy evaluated by isoconversional method suggested by Friedman; α is the conversion degree) obtained from non-isothermal experimental data and activation energy values, E_{iso}, obtained by applying the differential method to isothermal data simulated using non-isothermal kinetic parameters. According to this last criterion, the most probable mechanism of parchment oxidation consists in four successive steps. The contribution of the thermo-oxidation process in the parchment damage by natural aging is discussed.

Keywords Parchment · Thermo-oxidative degradation · Non-isothermal kinetics

Introduction

Among collagen-based materials, parchments contained in some heritage (historical or cultural) objects belong to the European culture. Therefore, the evaluation of the impact of environmental conditions on the physical and chemical properties of this material is important for damage identification and assessment in such objects. Parchment natural degradation at all levels of structural hierarchy (from molecular to microscopic levels) can be categorized according to the cause and the associated external manifestations in: chemical, mechanical, biological and physical damage [1]. The chemical damage of parchment is mainly due to hydrolysis, oxidation and some pollutants like sulfur dioxide and nitrogen oxides [1–4]. To investigate these kinds of degradation, some destructive, micro-destructive and non-destructive analytical techniques were applied. From the data obtained by application of these techniques, actions to ensure the preservation of parchments in the form of manuscripts, scrolls, book covers, and substrates for art works can be taken. Among the analytical techniques, the thermal analysis methods (TG/DTG, DTA, DSC, DMA, methods for shrinkage temperature

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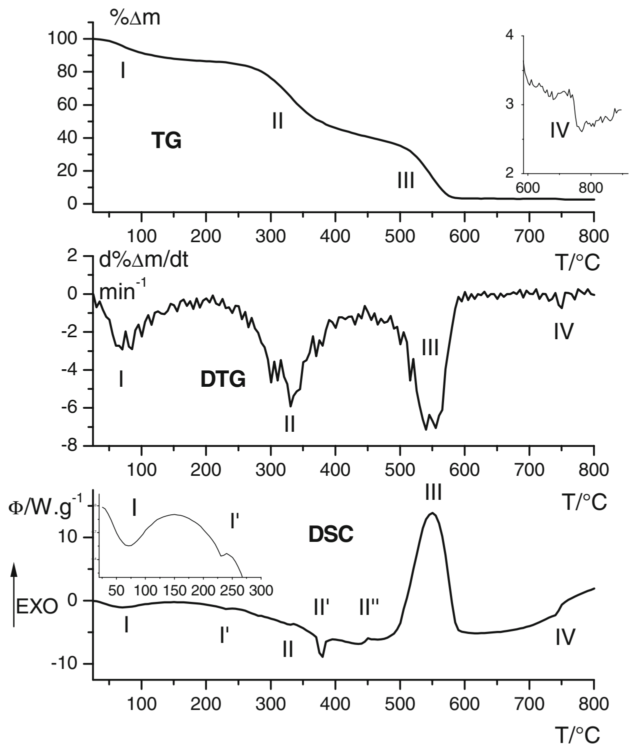


Fig. 1 TG, DTG and DSC curves for the investigated parchment, analyzed in static air atmosphere and the heating rate of 12.53 K min^{-1}

determination, thermo-microscopy, etc.) were used [5–21] to characterize the recently manufactured and old parchments and to reveal the changes in the parchment state occurring because of the natural or artificial aging.

The main objective of this work is to use of thermoanalytical data for evaluation of the mechanism and corresponding kinetic parameters of thermo-oxidative degradation of a recently manufactured parchment. The obtained results will be used for putting in evidence the contribution of oxidation with formation of volatile compounds on the damage of parchment stoked in normal environmental conditions.

Experimental

Material

Our experiments were carried out on a sort of a parchment recently manufactured by Leather and Footwear research Institute—Bucharest—Romania, from a goat skin. The analyzed samples were extracted from the same region of the parchment sheet. The shrinkage temperature of the parchment, determined by both Micro Hot Table method (MHT method) and DSC analysis of the sample immersed in water [18, 20], is $T_s = 58$ °C.

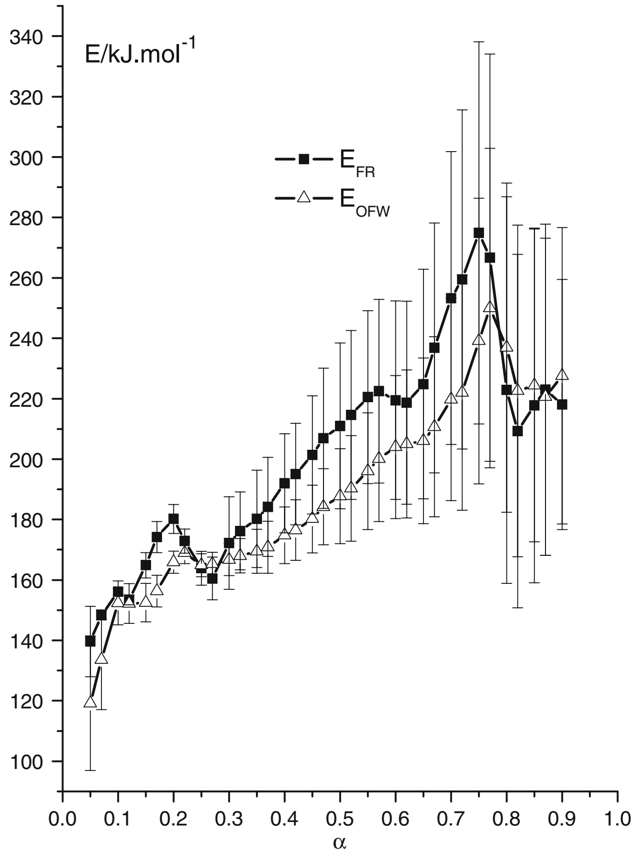


Fig. 2 Dependence of the activation energy evaluated by isoconversional methods on the conversion degree, for the process II

Thermal analysis

The heating curves (TG/DTG and DSC) of the goat parchment were simultaneous recorded with STA 490C apparatus produced by Netzsch—Germany, in static air atmosphere, in the temperature range 25–800 °C, and at following heating rates: 2.99; 4.96; 7.43; 9.96; 12.53 and 15.20 K min^{-1}. The mass of each analyzed sample was in the range 3.70–4.20 mg.

Processing of the experimental data

"Netzsch—Thermokinetics—A Software Module for the Kinetic Analysis of Thermal Measurements" was used for processing of non-isothermal data. The basic concepts of this program have been given in Ref. [22]. Recently [23–33] this program was used for the kinetic analysis of some non-isothermal data recorded at several heating rates.

The isoconversional differential method suggested by Friedman [34] (FR method) and the isoconversional integral method suggested independently by Ozawa [35], and Flynn and Wall [36] (OFW method) were applied for

Table 1 *F*-test on fit-quality

Nr.	Code	F_{exp}	F_{crit} (0.95)	f-act	Type 1	Type 2	Type 3	Type 4	Type 5
0	p:f,f,f,f	1.00	1.25	221	An	Fn	An	An	An
1	p:f,f,f,f	1.00	1.25	224	An	Fn	An	Fn	An
2	q:f,f,f	1.05	1.25	226	An	Fn	An	An	
3	t:f,f	1.08	1.25	224	An	Fn	An	Fn	
4	p:f,f,f,f	1.12	1.25	224	An	Fn	An	An	Fn
5	d:f	1.15	1.25	228	An	An			
6	t:f,f	1.33	1.25	227	An	Fn	An		
7	d:f	1.38	1.25	228	An	Fn			
8	d:f	1.62	1.25	228	Fn	An			
9	d:f	2.93	1.25	228	Fn	Fn			

evaluation of the dependence of the activation energy (*E*) on the conversion degree (α).

"Multivariate Non-linear Regression" program was applied for determination of the complex mechanism of the investigated process and the kinetic parameters characteristic for each reaction step.

Results and discussions

Figure 1 shows the simultaneous TG/DTG and DSC curves for the investigated parchment, recorded at 12.53 K min^{-1}; similar curves were obtained for all heating rates. They are qualitatively in agreement with the results previously reported for some collagen-based materials [11, 13, 14, 37–40]. The non-isothermal thermo-oxidative degradation of the parchment occurs through four successive processes accompanied by mass losses, denoted in TG and DTG curves by I, II, III and IV. In the first endothermic process I, the water contained by material is completely lost. The next step II is characterized by a small exothermic peak (II in DSC curve) and an endothermic peak (II' in DSC curve), and a complex DTG curve. According to the recent results obtained by chemiluminometric experiments with parchment in N_2 atmosphere [41], the process II is preceded by formation of solid hydroperoxides. The process III is exothermal one and consists in the oxidation of the solid compounds resulted in process II. The process IV is the decomposition of calcium carbonate traces that remained after the processing of goat skin performed for obtaining the parchment. Between the end of the process I and the beginning of process II, in the range where the mass loss is very small, an endothermic process denoted by I' occurs. This process, earlier detected by Okamoto and Saeki [42], and recently [19–21] put in evidence for pure collagen and collagen-based materials, could be explained by the biphasic amorphous-crystalline structure of collagen-based materials according to which the crystalline triple-helix is embedded into a amorphous matrix [20, 21]. Very recently [21], the data from Proton solid-state NMR, obtained for pure collagen, parchments and leathers, have lead to a three-phase model (rigid, inter-face, and mobile phase). Consequently, the process I' might be related to softening (melting) of the rigid (crystalline) part of parchment. Finally, between processes II and III, an exothermic process (denoted by II"), with a small change of sample mass, occurs. The later process could be the oxidation of the solid products resulting in process II to solid compounds, which will be decomposed and/or oxidized with release of volatile compounds.

The kinetic analysis was performed for the process II, characterized by a mass loss of 45.0 ± 1.1%. Only the experimental data corresponding to the heating rates 4.96; 7.43; 9.96; 12.53 and 15.50 K min^{-1} were processed by Netzsch Thermokinetics software. The data recorded at 2.99 K min^{-1} were used for checking the results of the kinetic analysis.

Model-free (isoconversional) estimation of the activation energy according to FR and OFW methods

The results obtained by application of FR and OFW methods are presented in Fig. 2. Both E_{FR} and E_{OFW} depend on the conversion degree, and exhibit absolute values of the relative standard deviation lower than 10% only for $0.05 \leq \alpha \leq 0.45$. The differences between E_{FR} and E_{OFW} values were explained [43, 44] by the relations that ground the model-free methods. In the following we will refer to results obtained by FR method that use the point values of the overall process rate and unlike OFW method does not include by integration the history of the system in the range 0–α.

Table 2 Non-isothermal kinetic and statistic parameters after non-linear regression through the most three probable mechanisms of the process II of thermo-oxidation of the investigated parchment

p:f,f,f,f with the kinetic models An-Fn-An-An-An		p:f,f,f,f with the kinetic models An-Fn-An-Fn-An		q:f,f,f with the kinetic models An-Fn-An-An	
Parameter	Value	Parameter	Value	Parameter	Value
log A_1/s^{-1}	14.535	log A_1/s^{-1}	12.138	log A_1/s^{-1}	11/607
E_1/kJ mol^{-1}	168.0	E_1/kJ mol^{-1}	150.0	E_1/kJ mol^{-1}	150.0
n_1	0.359	n_1	0.615	n_1	0.651
log A_2/s^{-1}	10.248	log A_2/s^{-1}	10.600	log A_2/s^{-1}	16.393
E_2/kJ mol^{-1}	138.0	E_2/kJ mol^{-1}	138.0	E_2/kJ mol^{-1}	214.0
n_2	0.822	n_2	0.882	n_2	0.922
log A_3/s^{-1}	16.674	log A_3/s^{-1}	16.590	log A_3/s^{-1}	20.173
E_3/kJ mol^{-1}	214.3	E_3/kJ mol^{-1}	214.3	E_3/kJ mol^{-1}	274.9
n_3	0.259	n_3	0.613	n_3	0.369
log A_4/s^{-1}	20.020	log A_4/s^{-1}	20.154	log A_4/s^{-1}	9.057
E_4/kJ mol^{-1}	274.9	E_4/kJ mol^{-1}	274.9	E_4/kJ mol^{-1}	160.0
n_4	0.803	n_4	2.000	n_4	0.172
log A_5/s^{-1}	7.641	log A_5/s^{-1}	9.057	FollReact 1	0.376
E_5/kJ mol^{-1}	160.0	E_5/kJ mol^{-1}	160.0	FollReact 2	0.100
n_5	0.081	n_5	0.129	FollReact 3	0.341
FollReact 1	0.077	FollReact 1	0.176		
FollReact 2	0.005	FollReact 2	0.065		
FollReact 3	0.538	FollReact 3	0.470		
FollReact 4	0.197	FollReact 4	0.140		

Statistical parameters			Statistical parameters			Statistical parameters		
Correlation coefficient	Durbin–Watson factor	*t*-critical (0.95; 221)	Correlation coefficient	Durbin–Watson factor	*t*-critical (0.95; 224)	Correlation coefficient	Durbin–Watson factor	*t*-critical (0.95; 226)
0.99970	2.567	1.962	0.99970	2.703	1.962	0.99969	2.493	1.962

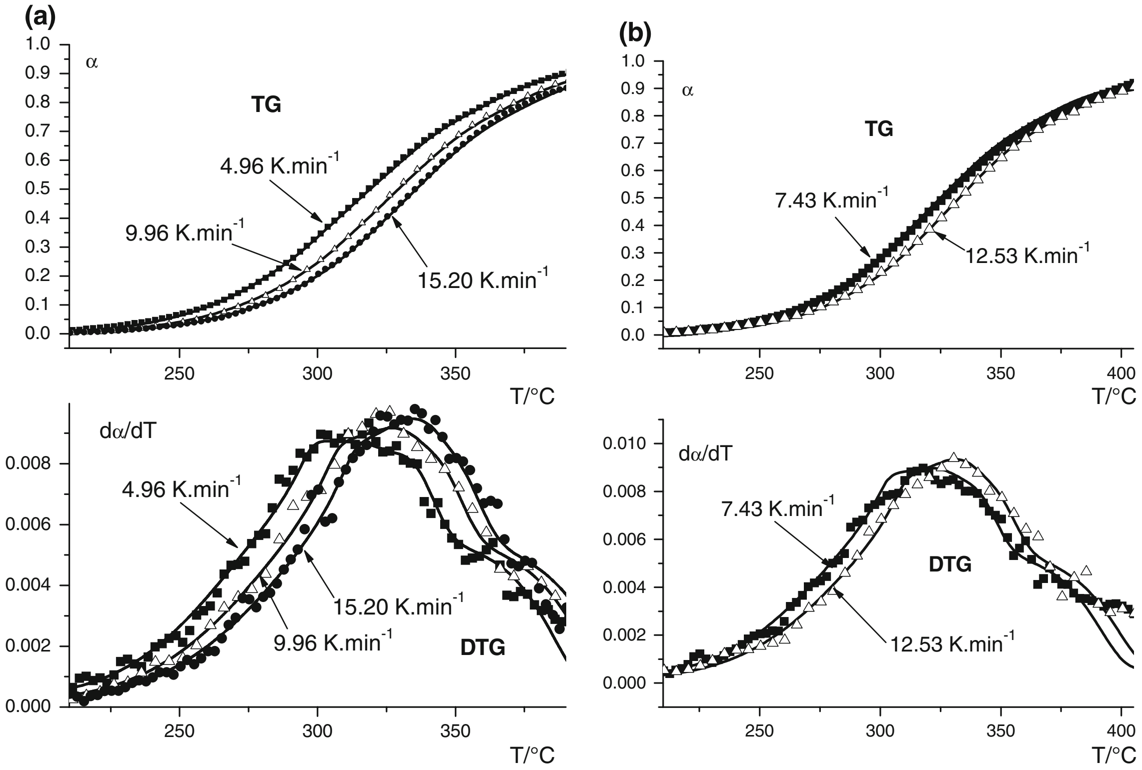


Fig. 3 Fit the measurements through four step mechanism q:f,f,f with conversion functions An-Fn-An-An. **a** 4.96; 9.96; 15.20 K min^{-1}, **b** 7.43; 12.53 K min^{-1}

Modeling as multiple-step reaction

The dependence of the activation energy on the conversion degree and the high absolute values of the standard deviation of E for $\alpha > 0.45$, evaluated by model-free methods show that the process II of thermo-oxidation of the investigated parchment is complex. The complexity of this process results also from the shapes of DTG and DSC curves corresponding to parchment oxidation in the temperature range 250–450 °C (see Fig. 1). In order to find the mechanism of this process and the corresponding kinetic parameters, we have been used “Netzsch Thermokinetics” program. The non-isothermal data recorded at the above mentioned heating rates were brought together during analysis and the relevant differential equations of the overall reaction rates are numerically solved and the kinetic parameters are iteratively optimized. The calculations were performed for the range of the conversion degree $0.05 \leq \alpha \leq 0.90$ and considering the following conversion functions:

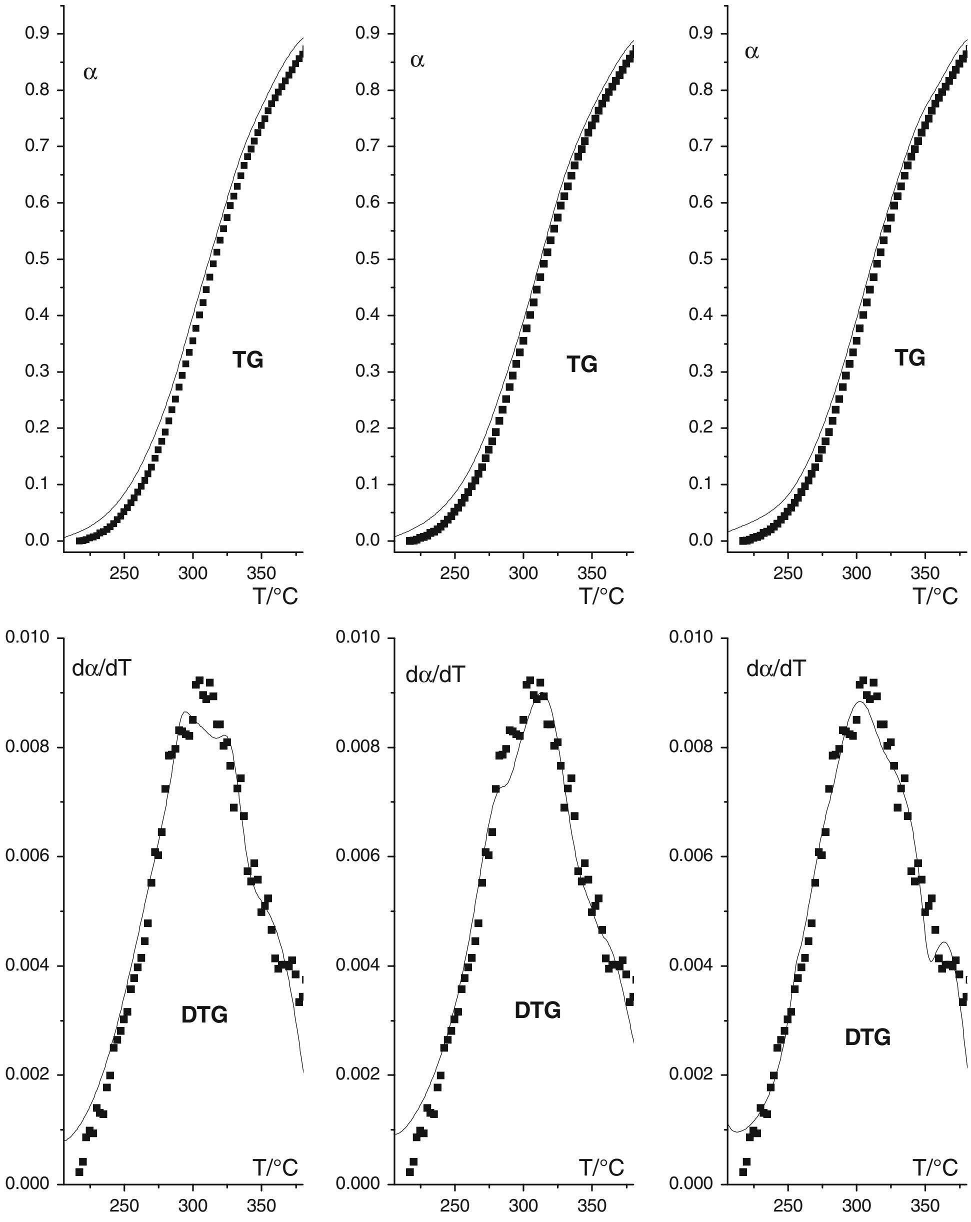
- reaction order model, Fn: $f(\alpha) = (1 - \alpha)^n$ (n is the reaction order);
- Avrami–Erofeev model, An: $f(\alpha) = n(1 - \alpha)[-\ln(1 - \alpha)]^{(1-1/n)}$ (n is a constant parameter).

The following schemes (mechanisms) of process II were also taken into account:

- scheme coded by d:f: $A - 1 \rightarrow B - 2 \rightarrow C$
- scheme coded by t:f,f: $A - 1 \rightarrow B - 2 \rightarrow C - 3 \rightarrow D$
- scheme coded by q:f,f,f: $A - 1 \rightarrow B - 2 \rightarrow C - 3 \rightarrow D - 4 \rightarrow E$
- scheme coded by p:f,f,f,f: $A - 1 \rightarrow B - 2 \rightarrow C - 3 \rightarrow D - 4 \rightarrow E - 5 \rightarrow F$

(the codifications are those used in “Netzsch Thermokinetics” program; A, B, C, D, E and F are solid compounds; 1; 2; 3; 4 and 5 denote the mechanism steps)

Table 1 lists the F-test on Fit-Quality of the considered mechanisms. In the following, only the first three mechanisms in the order of decreasing of the F-test on Fit-Quality will be considered. The corresponding kinetic parameters are listed in Table 2. For these mechanisms, both the experimental TG and DTG points lie practically on the regenerated curves (see for example Fig. 3 in which the regenerated TG and DTG curves were calculated for the q:f,f,f—An-Fn-An-An mechanism and the parameters listed in Table 1). As results from Fig. 4, for all above mentioned mechanisms and the heating rate of 2.99 K min^{-1} that was not considered for evaluation of kinetic



q:f,f,f-AnFnAnAn **p:f,f,f,f-AnFnAnFnAn** **p:f,f,f,f-AnFnAnAnAn**

Fig. 4 Calculated TG and DTG curves (__) and the experimental points (■) for the heating rate of 2.99 K min^{-1}

parameters, the experimental TG and DTG points lie practically on the corresponding regenerated curves.

In a previous paper [32] we suggest, as a necessary criterion for validity of the determined mechanism and the corresponding kinetic parameters, the good agreement between $E_{FR} = E_{FR}(\alpha)$ obtained from non-isothermal experimental data and $E_{iso} = E_{iso}(\alpha)$obtained by applying the differential method to isothermal data simulated using non-isothermal kinetic parameters. In order to check this criterion, the isothermal data were calculated using parameters listed in Table 2, for seven temperatures in the range 210–240 °C, with a step of 5 °C, and the dependence of E_{iso} vs. α was determined for each of three above-mentioned mechanisms. E_{iso} vs. α, E_{FR} vs. α, and $e\% = 100 \times (E_{iso} - E_{FR})/E_{FR}$ curves are shown in Fig. 5. For put in evidence the best agreement between E_{iso} and E_{FR}, the values of „mean absolute relative difference" between these quantities (*ARD),* given by relation:

$$ARD = \frac{100}{N}\sum_{N}\left|\frac{E_{iso} - E_{FR}}{E_{FR}}\right|$$

($N =$ number of considered values of the activation energy) were evaluated for each mechanism and two ranges of conversion degree, namely $0.05 \le \alpha \le 0.80$ and

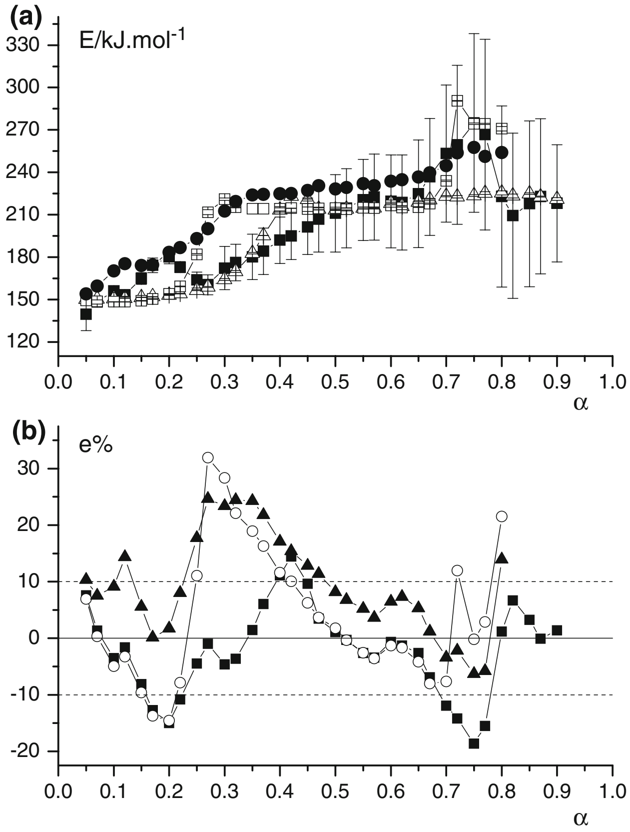


Fig. 5 **a** Comparison between the values of E obtained by FR method from non-isothermal experimental data and those evaluated using isothermal data calculated using the kinetic parameters corresponding to most probable three mechanisms: ■ E_{FR}; Δ E_{iso} for q:f,f,f—An-Fn-An-An; □ E_{iso} for p:f,f,f,f—An-Fn-An-Fn-An; ● p:f,f,f,f—An-Fn-An-An-An. **b** $e\% = 100 \times (E_{iso} - E_{FR})/E_{FR}$ vs. α. ■ q:f,f,f—An-Fn-An-An; o p:f,f,f,f—An-Fn-An-Fn-An; ▲ p:f,f,f,f—An-Fn-An-An-An

Table 3 ARD values for E_{iso} and the first three mechanisms in order of decreasing of F-test on Fit Quality

Mechanism	α range	ARD (%)
p:f,f,f,f—An-Fn-An-An-An	$0.05 \leq \alpha \leq 0.80$	10.50
	$0.05 \leq \alpha \leq 0.45$	14.02
p:f,f,f,f—An-Fn-An-Fn-An	$0.05 \leq \alpha \leq 0.80$	9.33
	$0.05 \leq \alpha \leq 0.45$	12.81
q:f,f,f—An-Fn-An-An	$0.05 \leq \alpha \leq 0.80$	6.43
	$0.05 \leq \alpha \leq 0.45$	6.89

$0.05 \leq \alpha \leq 0.45$. The last range corresponds to absolute values of relative standard deviation lower than 10%. According to the results listed in Table 3, the minimum values of *ARD* were obtained for the mechanism q:f,f,f—An-Fn-An-An. Consequently, the first process of thermo-oxidation of the investigated parchment is satisfactory described by this mechanism and the corresponding kinetic parameters.

In the following we will show that the above presented results can be used for explaining the results reported in a previous paper [45], according to which TG, DTG and DSC curves of both the initial and air-aged goat parchment at 195 °C for 2 h, characteristic for thermo-oxidative processes, exhibit very closed parameters. This statement, the observed effect of thermal aging on the dehydration process and SEM study lead to the conclusion that thermal aging in air of parchment does not affect the thermo-oxidative stability, but determines the morphology and hydrothermal properties changes. This conclusion could be associated with the small value of the mass loss calculated for the pair temperature-time 195 °C—2 h, using the above given kinetic parameters corresponding to q:f,f,f—An-FnAnAn mechanism (2.33%; $\alpha = 0.052$). However, the use of the results of kinetic analysis of process II for prediction of thermal lifetime (L) corresponding to a certain mass loss as an endpoint criterion leads to unrealistic very high value of L; e.g. for 2.25% mass loss ($\alpha = 0.050$) and 40 °C, $L = 41200$ year. This result put in evidence the high oxidative stability of parchment, but there are three major irreversible degradation paths for parchment: denaturation, hydrolysis and oxidation. According to our results, the thermo-oxidation with formation of volatile compounds is not the main process that determines the damage of parchments by natural aging.

Conclusions

1. The processes which occur in the progressive heating in air of a goat parchment were shown by thermal analysis (TG, DTG and DSC).
2. Kinetic analysis of the first process of thermo-oxidation was performed by isoconversional (model-free) methods and "multivariate non-isothermal regression" program applied to the non-isothermal data recorded at five heating rates.
3. In order to find the mechanism of the investigated process and to determine the corresponding kinetic parameters, there were applied the F-test on Fit Quality for TG curves, and the criterion according to which the most probable process mechanism corresponds to the best agreement between $E_{FR} = E_{FR}(\alpha)$ obtained from non-isothermal experimental data and activation energy values $E_{iso} = E_{iso}(\alpha)$ obtained by applying the differential method to isothermal data simulated using the determined non-isothermal parameters. These criteria lead to q:f,f,f mechanism with the kinetic models An-Fn-An-An, which is suitable for predictions.
4. The obtained results put in evidence that the oxidation process with formation with volatile compounds has a

low contribution in the damage of parchments stocked in normal environmental conditions.

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