NPK Analysis of the Thermal Degradation of Decabromodiphenylether

MIHAI DUMITRAS[1], DAN MAFTEI[1], ANTON AIRINEI[2], NITA TUDORACHI[2], ALIN CONSTANTIN DIRTU[1]*

[1] Al. I. Cuza University of Iasi, Department of Chemistry, Romania, 11 Carol I Blvd., 700506, Iasi, Romania
[2] Petru Poni Institute of Macromolecular Chemistry, Iasi, 41A Grigore Ghica Voda Al., 700487, Iasi, Romania

This study aims to investigate the thermal degradation behavior of decabromodiphenyl ether (BDE 209) by simultaneous TG/DTA under various conditions. Due to low volatility, high elution temperatures are needed when applying chromatographic techniques for this class of flame retardants (FR), resulting in thermal degradation affecting analysis results, but no systematic study has been reported. Kinetic analysis was performed by the non-parametric (NPK) method, and in correlation with evolved gas analysis (EGA) information and molecular modeling results, provided valuable insight into the kinetics and mechanism of BDE 209 thermal degradation. The conclusions were aimed at designing proper specific GC analytical methods for the selected FRs and serving for a better estimation of the human exposure to such compounds.

Keywords: brominated flame retardants, thermal degradation, TG-DTA, nonparametric kinetics

The scientific literature related to the estimation of human exposure to brominated flame retardants (BFRs) is rapidly growing [1]. For investigating BFRs' presence in matrices related to human exposure GC-MS instruments are generally used [2]. However, given the relatively low volatility of BFRs, high elution temperatures are needed when applying conventional chromatographic techniques for investigating their presence in matrices related to human exposure to these compounds, such as indoor dust samples or food items, leading to thermal degradation that generates under-estimation of human exposure to such compounds [2]. No study on the thermal degradation of this class of compounds by proper thermoanalytical methods has been reported in the literature, while only a few papers report basic thermal degradation data for polybrominated diphenyl ethers [3,4]. We have investigated thermal degradation behavior of decabrominated diphenyl ether (BDE 209), a FR which accounts for more than 90% of the total BDEs reported from indoor dust samples from Eastern Romania [5], by simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) under different atmospheres (nitrogen, helium and air) and with different heating rates. Degradation onset was found to occur at rather low temperatures, around 300 ᵒC.

Classical methods of thermal analysis, also known as model-fitting methods, postulate a kinetic model and estimate the values of model parameters by fitting on experimental data [6]. Some of the most used such methods include Freeman-Carroll [7], Coats-Redfern [8], Fatu [9], Reich-Levi or the initial rate method [10]. The kinetic models employed are empirical or semi-empirical [11] and in literature there is a collection of so-called *recommended* equations used to describe a wide variety of processes [12] such as nucleation and crystal growth, interfacial, diffusion controlled, power-law or chemical reaction models. It has been shown that this approach is a strictly operational one and the obtained kinetic parameters have in general no physical meaning [13-15].

Isoconversional methods, also known as model-free methods [16], manage to overcome the necessity to postulate a kinetic model by relying on thermo-analytical experimental data obtained at various heating rates, allowing for an estimation of the kinetic parameters to be made before the model is identified. Thus, the errors implied by misidentification of the *correct* kinetic model on the kinetic parameters are avoided. Still, they rely on several drastic approximations [17], that narrows down their applicability, such as the *single step kinetics approximation* that requires all the kinetic parameters (activation energies and pre-exponential factors included), as well as the conversion function, to be invariants over the whole experimental range of temperature and conversion degree. This leads to a logical trap [17], since these methods often outputs *variable activation energies* that varies with the conversion degree, leading to questions about the mathematical validity of this approach.

Non-parametric kinetic analysis [18-20] (NPK) represents a completely different approach on kinetic modeling of thermo-analytical data. It does not involve any *a priori* model, but instead it uses a system of submatrices obtained from a set of thermogravimetric curves recorded at various heating rates. It allows, by algebraic manipulation of the experimental data matrix, the decoupling of the two variables: temperature and conversion degree, without any assumption on the form of the reaction rate dependence on these variables. This allows for a superior generalization degree, since it does not require any approximation to be made. NPK also allows reconstructing isothermal data from non-isothermal experiments. Despite its obvious advantages, the method is presently seldom used in analyzing thermoanalytical data, due to its complexity and the volume of calculation involved [21].

Kinetic analysis of the recorded non-isothermal degradation data was performed by the non-parametric (NPK) algorithm, which allows for some new kinetic aspects of the degradation process to be obtained and provides an accurate description of the process that can be relied upon in a subsequent mechanistic modeling of the degradation reactions. Investigation of the obtained isoconversional and isothermal vectors allowed for two parallel major degradation pathways to be identified, corresponding to two different bond breakage patterns. The relative importance of the two reaction pathways in the global degradation mechanism were found to be temperature-dependent, correlated to the obtained variation of the global activation energy with temperature. These findings are supported by molecular modeling

* email: alin.dirtu@chem.uaic.ro; Phone: 0748 353 824, 0232 20 1309

results, providing additional insight for interpreting GC experimental results and serving as a basis for designing proper analytical methods for BFRs.

Experimental part

The decabromodiphenyl ether (BDE 209) in solid form (99.0% purity) submitted to analysis was supplied by Dr. Ehrenstorfer GmbH, Germany. Thermal degradation experiments were performed on a Netzsch STA 449 F1 Jupiter with simultaneous recording of TG and DTA, using alumina crucibles. A constant flow of 40 mL/min of gas (nitrogen, helium and air, respectively) was used. Linear heating rates of 2, 5, 10, 15 and 20 K/min were used, with sample mass of about 4 mg. Temperature and sensitivity calibration (DTA) was performed using Netzsch certified standards. Matrix interpolation was performed using OriginPro 9.0 (OriginLab), while singular value decomposition (SVD) operations on matrices were performed using Mathcad 14 (Mathsoft).

Results and discussions

Thermal degradation experiments

The TG/DTG curves for BDE 209 thermal degradation under different atmospheres (nitrogen, helium and air) are presented in figure 1, while figure 2 depicts the corresponding DTA recordings. In figures 3 and 4, the TG/DTG and DTA curves, respectively, are illustrated for BDE 209 degradation under nitrogen flow at different heating rates. Analyzing the TG/DTG curves it can be seen that thermal degradation of BDE 209 occurs in a single step, with 100% weight loss, regardless of heating rate and atmosphere, with an initial degradation temperature of 310 ^{0}C, slightly shifted towards higher values with increasing heating rate (316 ^{0}C for 20 K/min).
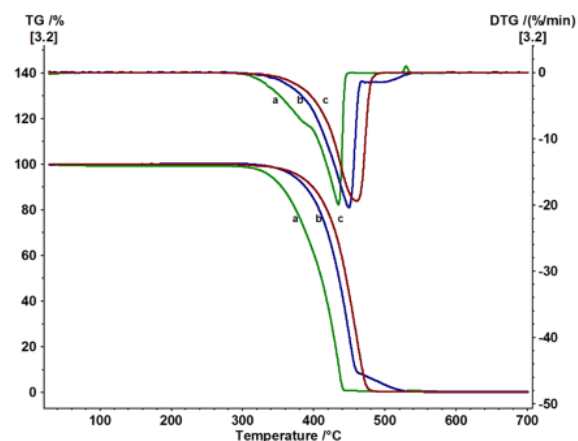

Fig. 1. TG/DTG curves for BDE 209 at 10 K/min in different atmospheres: helium (a), nitrogen (b) and air (c)
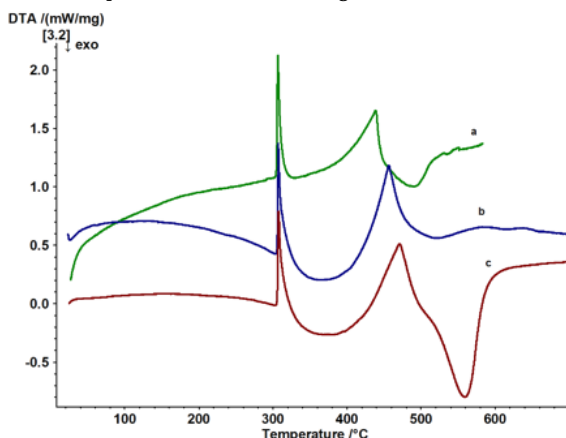

Fig. 2. DTA traces for BDE 209 at 10 K/min in different atmospheres: helium (a), nitrogen (b) and air (c)

DTA recordings suggest a partial overlapping of melting (the endothermic peak at 304°C, regardless of heating rate) and thermal degradation in the initial stages, followed by a second endothermic degradation step at higher temperatures that shifts with increasing heating rate (438, 456 and 471°C for 2, 10 and 20 K/min, respectively). This hypothesis is supported by the fact that the first peak is completely reversible if consecutive heating and cooling cycles are run, as shown in figure 5. For the specific melting enthalpy a value of 34.6 J/g was found by integrating the DTA melting peak for multiple runs and averaging the results.

Marked asymmetry and an inflexion point are noted in the DTA degradation peak, suggesting a change in the reaction mechanism after maximum degradation rate is attained, without any correspondence in the TG curves. As DTA and TG measurements are based on different fundaments, this apparent disagreement does not necessarily have a physical significance. DTA is much more sensitive than TG and the inflexion could indicate a variation in the degradation mechanism, as it is also observed in DTG (figs. 1 and 3) and, as it will be shown later, in the variation of the apparent activation energy with temperature.
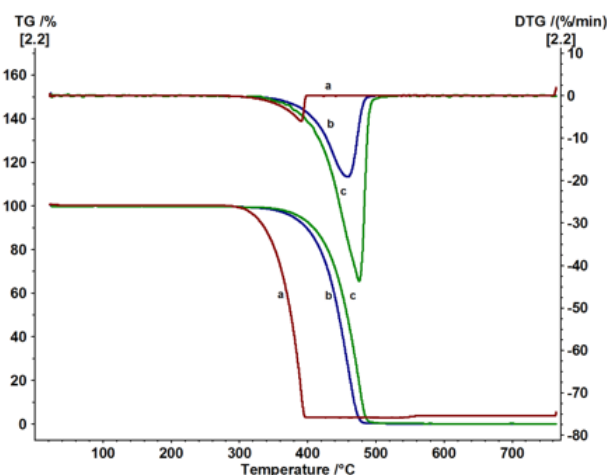

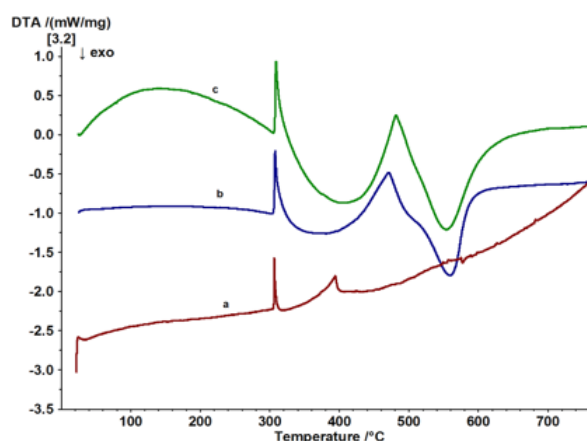Fig. 3. TG/DTG curves for BDE 209 in nitrogen at 2 (a), 10 (b) and 20 (c) K/min

Fig. 4. DTA recordings for BDE 209 in nitrogen at 2 (a), 10 (b) and 20 (c) K/min

NPK analysis

For the kinetic analysis of the TG data, the $T(t)$ and $m(T)$ dependencies provided by the thermo balance were normalized as $\alpha(T)$, where T is sample temperature, t is the time passed since the beginning of the degradation, m is sample mass and α is the conversion degree, defined as:
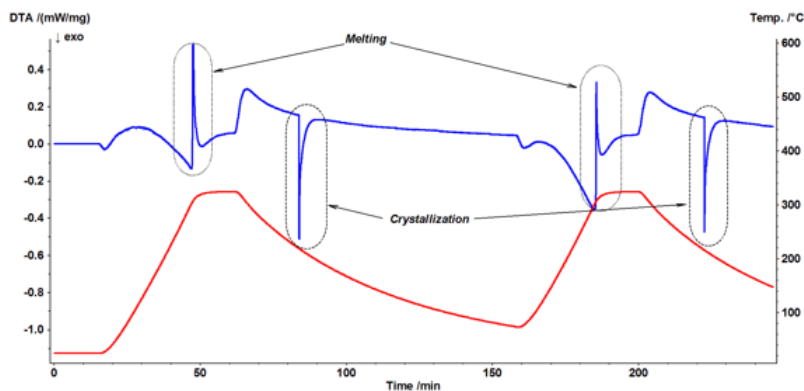
Fig. 5. DTA curve for BDE 209 in nitrogen at 10 K/min, for two consecutive heating/cooling cycles from 25 to 320 °C
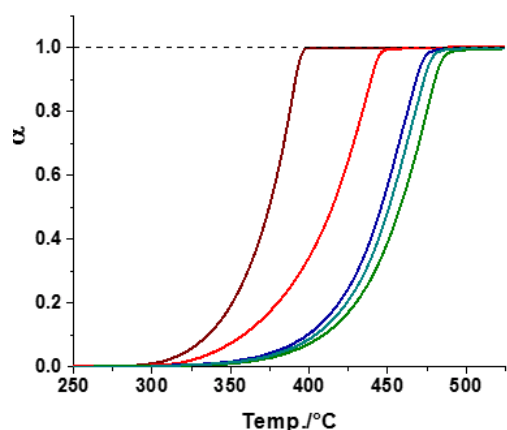

Fig. 6. Dependence of conversion degree (α) on temperature from TG data for BDE 209 in nitrogen at 2, 5, 10, 15 and 20 K/min (from left to right)

$$\alpha(T) = \frac{(m_0 - m_\infty) - (m(T) - m_\infty)}{m_0 - m_\infty} = \frac{m_0 - m(T)}{m_0 - m_\infty} \quad (1)$$

where m_0 is initial sample mass and m_∞ is the residue (sample mass after complete degradation). The obtained curves are presented in figure 6.

We shall define the reaction rate v as the first time derivative of α:

$$v = \frac{d\alpha}{dt} = -\frac{1}{m_0 - m_\infty}\frac{dm}{dt} \quad (2)$$

Obviously, the reaction rate is a two-variable function, as it depends on temperature and on conversion degree. The reaction rate dependence on temperature and on conversion degree along the experimental TG curves is depicted in figure 7.

The NPK algorithm [18-21] starts from the well-known equation relating the reaction rate to its variables T and α:
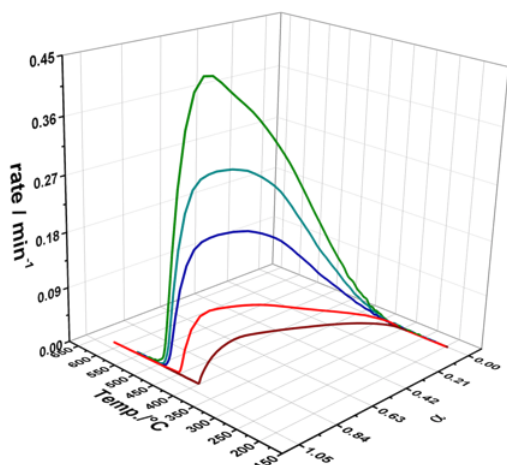

Fig. 7. Reaction rate dependence on temperature and conversion degree along the experimental curves

$$\frac{d\alpha}{dt} = F(T, \alpha) \quad (3)$$

The separability of the two variables, an essential condition in any other method of non-isothermal kinetic analysis, is expressed as:

$$F(T, \alpha) = k(T)f(\alpha) \quad (4)$$

but it does not have to be postulated here. If the condition is met, this fact arises naturally from calculation, and the NPK method allows testing the validity of the above equation point by point, along the entire course of the degradation process.

Based on equation (3), the reaction rate can be represented as a three-dimensional surface with variables T and α, that can be discretized as a matrix R (N x M) whose elements are the reaction rate for constant α (on rows) and for constant T (on columns).

$$R = \begin{bmatrix} F(\alpha_1, T_1) & \cdots & F(\alpha_1, T_M) \\ \vdots & \ddots & \vdots \\ F(\alpha_N, T_1) & \cdots & F(\alpha_N, T_M) \end{bmatrix} \quad (5)$$

Singular value decomposition (SVD) of R provides a set of three matrices: U (M x N orthogonal), W (N x N diagonal, whose elements are the singular values of M) and V (N x N orthogonal) that allows the original matrix to be reconstructed:

$$R = U \times W \times V^T \quad (6)$$

If the conversion and temperature functions are independent, the matrix R is the scalar product of two vectors, $f(\alpha)$ and $k(T)$. As a result, only the first columns of the matrices U and V, namely u (isothermal vector) and v (isoconversional vector), are needed to reconstruct the original matrix M. In this case, only the first singular value of M, respectively the first element of the diagonal matrix W, will be different from zero.

$$R = u \times w \times v^T \quad (7)$$

So, the NPK algorithm allows testing the validity of the condition in equation (4) by analyzing the singular values of R. The isothermal and isoconversional vectors express the influence of the variables α and T, respectively, over the reaction rate. The values of the conversion and temperature functions, $f(\alpha)$ and $k(T)$, at the grid points (α, T) where the discretization expressed in equation (5) has been made and can be directly computed from the two vectors provided by SVD:

$$f(\alpha) = [u_1, u_2, \dots u_N] \quad (8)$$

$$k(T) = [w_1 v_1, w_2 v_2, \dots w_1 v_M] \quad (9)$$

where w_1 represents the first singular value of M.

After computing the isothermal and isoconversional vectors, the nature of the $f(\alpha)$ and $k(T)$ functions can be investigated directly. They can also be used for fitting in mechanistic kinetic modelling [21].
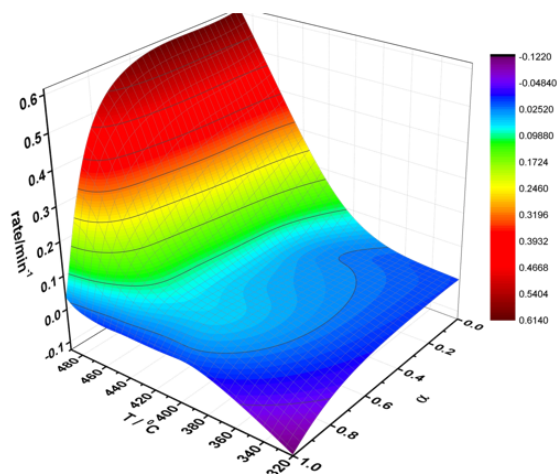
Fig. 8. Reaction rate surface obtained by thin plate spline multivariate interpolation, with a grid resolution of 500 pts (α) X 170 pts (T)

Fig. 10. Isothermal vector for BDE 209 thermal degradation

Following this procedure, the experimental data in figure 7 were used to construct the three-dimensional surface representing the reaction rate by thin plate spline multivariate interpolation, as depicted in figure 8. As it can be seen from figure 6, experimental data are available on a restricted range of temperature and conversion degree. To avoid using extrapolated data outside the experimental range, adaptive NPK was used [19,21] by extracting a set of partially overlapped submatrices that were then submitted to SVD, each submatrix providing a pair of individual vectors (u and v). In all cases the first singular value exceeded 90% of the sum of all sv's, proving the separability of T and α. Because SVD is unique up to a multiplication scalar, the individual vectors obtained were shifted vertically with respect to each other and they were scaled based on a continuity criterion [8] to construct the isothermal and isoconversional vectors.

The isoconversional vector is presented in the Arrhenius-type plot in figure 9, as $\ln(k)$ vs $(RT)^{-1}$. Two thermal degradation regimes are made evident, with a turning point at 405°C and different apparent activation energies: an initial stage between 310 and 400°C, with $E_a = 60.8$ kJ/mol, followed by a second stage between 410 and 490°C, with $E_a = 185.9$ kJ/mol, each exhibiting remarkable linearity in these coordinates. The transition from one regime to the other is continuous, with a continuously varying apparent activation energy. These observations indicate that competitive reaction pathways coexist, with different contributions to the global kinetics of the degradation, as previously reported for other systems [22-24].
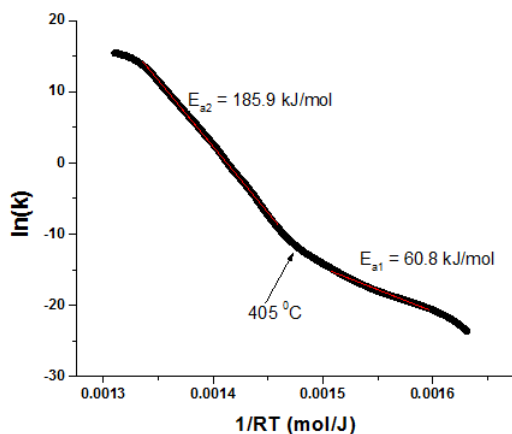
The balance between the contributions of parallel reaction paths to global kinetics is expected to shift with temperature since the effective rate constant is a linear combination of the rate constants of the individual pathways, and the temperature dependence of the degradation process could be modelled as a sum of contributions, each of them being of Arrhenius type:

$$k_{effective}(T) = f_1 A_1 exp\left(-\frac{E_{a1}}{RT}\right) + f_2 A_2 exp\left(-\frac{E_{a2}}{RT}\right) \quad (10)$$

where f_1 and f_2 represent the probability of each pathway, respectively, depending on temperature and composition.

An analysis of the conversion function (figure 10) reveals similar behaviour, with two different reaction regimes separated by a transition range between 0.4 and 0.65 conversion degree values. A detailed analysis of the nature of the isothermal vector would require a mechanistic approach and is beyond the scope of this study, but some information can be extracted by fitting with the Sestak-Berggren equation [25]. As noted in figure 10, the initial degradation regime is very close to zero order kinetics, indicating a predominantly heterogeneous process. Non-integer coefficients obtained in the second stage are indicative of complex degradation mechanism.

These findings suggest that in the initial stage evaporation and thermal scission of molecules from the surface with vaporisation of the fragments occurs simultaneously. With increasing temperature an alternate reaction route with higher energy barrier, probably involving intermolecular chain transfer and occurring in the entire mass of the sample, becomes predominant and eventually takes control over the global kinetics.

In order to elucidate the degradation mechanism, the results of the NPK analysis will be correlated to a detailed analysis of the degradation product distribution and to molecular modelling results in a subsequent study.

Conclusions

BDE 209 undergoes thermal degradation in a single step, regardless of the heating rate or atmosphere, with an initial degradation temperature of 310 °C and a partial overlapping of melting and thermal degradation in the initial stages.

The degradation rate dependencies on temperature and conversion degree are separable, with more than 90% of weight loss occurring through a single process. The isoconversional and isothermal vectors were computed, revealing two reaction stages separated by a transition regime. The results suggested that, even if the degradation occurs in a single step, the reaction mechanism modifies as the degradation advances.

Fig. 9. Arrhenius-type plot of the isoconversional vector for BDE 209 thermal degradation

The conclusions of the thermal degradation study, correlated with EGA-FTIR/MS data and molecular modeling results, provide additional insight for interpreting GC experimental results and may serve as a basis for designing proper GC analytical methods for the selected FRs.

References

1.DIRTU, A.C, IONAS, A.C., MALARVANNAN, G., COVACI, A., Transformation Products of Emerging Contaminants in the Environment. John Wiley & Sons Ltd, Chichester, UK, 2014, p. 545.
2.DIRTU, A.C, ABDALLAH, M.A.E., COVACI, A., TRAC-Trend. Anal. Chem, **43**, 2013, p. 189.
3.GHANEM, R., DELMANI, F. A., J. Anal. Appl. Pyrolysis, **98**, 2012, p. 79.
4.TAO, H.; NAKAZATO, T., Bunseki Kagaku, **58**, no 5, 2009, p. 363.
5.DIRTU, A.C., ALI, N., VAN DEN EEDE, N., NEELS, H., COVACI, A., Environ. Int., **49**, 2012, p. 1.
6.BROWN, M.E. (editor), Handbook of Thermal Analysis and Calorimetry: Principles and Practice, vol 1, Elsevier, Amsterdam, 1998, p. 50.
7.FREEMAN, E.S., CARROLL, B., J. Phys. Chem., **62**, 1958, p. 394.
8.COATS, A.W., REDFERN, J.T., Nature, **201**, 1964, p. 68.
9.FÃTU, D., Algorithm and software for evaluating the kinetic parameters from DTA data; Proceedings of the VIIth Conference on Physical Chemistry, Bucharest, 1994, p. 21.
10.SHARP, J. H., Differential Thermal Analysis; R.C. McKenzie Academic Press, London; vol. II, 1972, p. 121.
11.MAMLEEV, V., BOURBIGOT, S., LE BRAS, S., DUQUESNE, S., SESTAK, J., Phys. Chem. Chem. Phys., **2**, 2000, p. 4708.
12.GALWAY, A. K., BROWN, M. E., Thermal Decomposition of Ionic Solids, Elsevier, Amsterdam, 1999, p. 23.
13.GALWAY, A. K., Thermochim. Acta, **413**, 2004, p. 139.
14.BUDRUGEAC, P., SEGAL, E., J. Therm. Anal. Calorim., **62**, 2000, p. 227.
15.HEAL, G.R., Thermochim. Acta, **426**, 2005, p. 23.
16.VYAZOVKIN, S., Thermochim. Acta, **355**, 2000, p. 155.
17.SIMON, P., J. Thermal Anal. Calorim., **82**, 2005, p. 651.
18.SERRA, R., NOMEN, R., SEMPERE, J., Thermochim. Acta, **316**, 1998, p. 37.
19.SERRA, R., NOMEN, R., SEMPERE, J., J. Thermal Anal. Calorim., **52**, 1998, p. 933.
20.SEMPERE, J., NOMEN, R., SERRA, R., SORAVILLA, J., Thermochim. Acta, **388**, 2002, p. 407.
21.SEMPERE, J., NOMEN, R., SERRA, E., SEMPERE, B., Hot Topics Thermal Anal. Calorim., **9**, 2013, p. 351.
22.LEDETI, I., VLASE, G., VLASE, T., MURARIU, M., TRANDAFIRESCU, C., SOICA, C., SUTA, L. M., DEHELEAN, C., LEDETI, A.,Rev. Chim.(Bucharest), **67**, no. 3, 2016, p. 549.
23.STANESCU, P.O., TURTURICA, G., ANDREI, M., DRAGHICI, C., VULUGA, D.M., ZAHARIA, A., SARBU, A., TEODORESC, M., Mat. Plast., **52**, no. 2, 2015, p. 193.
24.NICOLESCU, L.C., TITA, B., JURCA, T., MARIAN, E., TITA, D., Rev. Chim.(Bucharest), **66**, no. 11, 2015, p. 1802.
25.SIMON, P, Thermochim. Acta, **520**, 2011, p. 156.