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Characterization and kinetic analysis of the thermal decomposition of 2-oxy-4,6-dinitramine-*s*-triazine in non-isothermal conditions

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Abstract

The compound 2-oxy-4,6-dinitramine-*s*-triazine (DNAM) is a nitrated derivative of 2,4,6-triamine-*s*-triazine that, due to its energetic properties, is a candidate substance for energetic formulations. The thermal decomposition of DNAM and preliminary information on the exothermic reaction kinetics were studied by simultaneous thermal analysis in non-isothermal conditions. The Arrhenius parameters were estimated according to well-established methods but emphasis is given on statistical analysis of the correspondent regression procedures. DNAM presents good thermal stability in a wide temperature range below its exothermic decomposition that starts, according to the heating rates employed, above 473 K. The results of the kinetic analysis are critically discussed taking into account the complexity of the exothermic reaction, its relation with the heating rate, and some problems that are typical in the reaction kinetics of solids. © 1997 Elsevier Science B.V.

Keywords: Arrhenius parameters; Simultaneous thermal analysis (DSC/TGA); Thermal decomposition ; 2-oxy-4,6-dinitramine-*s*-triazine

1. Introduction

The compound 2-oxy-4,6-dinitramine-*s*-triazine (dinitroammeline, DNAM) is a nitrated derivative of 2,4,6-triamine-*s*-triazine (melamine) that was isolated for the first time by Cason [1] in 1947. Four years later Atkinson [2] reported further results but the characterization of the product remained incomplete. More recently, the characterization of DNAM was reinvestigated and improved, and its potential as a candidate substance to be used in propellant formulations was evaluated [3,4].

The thermal characterization is one of the most relevant steps in the study of new substances with applications in the energetic materials field. A detailed knowledge of the thermal behavior of each component is necessary, both for safety reasons and for a better prediction and/or description of the thermochemistry of energetic formulations. Twenty years ago Collins and Hans [5] have reviewed the application of thermal analysis techniques to the characterization of explosives. At that time they had anticipated an increasing interest in these techniques. The last two decades have

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confirmed that point of view and thermal analysis (DSC, DTA, TGA, etc.) has gained an increasing number of users in the material science.

However, the proliferation of thermal analysis studies, viewed as a whole, has led to some drawbacks. That is particularly clear in quantitative analysis of non-isothermal studies to obtain solid state decomposition kinetic parameters. Thermal analysis experiments conducted in non-isothermal conditions present several practical advantages when compared with isothermal studies and have been widely used and discussed [6]. Nevertheless, the non-isothermal kinetics of solid decomposition processes involves several assumptions due to the fact that some concepts commonly used are derived from the kinetics of homogeneous systems in the 'classical' sense. That is, the determination of reliable solid-state decomposition kinetic parameters is not trivial and conclusions are to be drawn cautiously. This problem has been frequently ignored and consequently many uncritical kinetic data have appeared in the literature. Fortunately this subject has deserved the attention of several authors (e.g. [6–9]) who have criticized, in a constructive way, the situation of the kinetics studies by means of thermal analysis in non-isothermal conditions and underlined the need to establish reliable procedures concerning the kinetic analysis of solid decomposition thermoanalytical data.

Some important aspects in thermal analysis practice are still being ignored, namely, the statistical treatment of thermoanalytical data. Indeed, thermal analysis being an experimental technique, involving the measurement of some set of variables, usually to find out dependencies between them, it is surprising that the use of statistical analysis methods has been so neglected and consequently not accounted in many papers (at least in an explicit way). When new materials are studied by means of thermal analysis, namely, to obtain the related solid-state decomposition kinetic parameters, and when no other data for comparison purposes are available, a careful data treatment is desirable. The sources of errors in kinetic analysis of thermal analytical data are various and can occur at different levels, from the experimental measurements to the mathematical modelling of the process. In view of so many uncertainties, it is good practice to make use of some statistical tools in order to conclusively demonstrate causal relations between variables. This methodology does not necessarily ensure the accuracy (reliability) of the obtained kinetic parameters since there are many physical factors that are difficult to identify quantitatively that should be taken into account. However, it can be very useful for uncovering hidden structures in the data and thus in clarifying the final conclusions.

In this work the thermal characterization and kinetic analysis of the decomposition of 2-oxy-4,6-dinitramine-*s*-triazine in non-isothermal conditions are presented. Due to the absence of published data on this subject and also due to the inevitable uncertainties associated with the kinetic analysis of solid decomposition processes, an attempt is made to give a critical sense in the explanation of the obtained results.

2. Theory

The most common methods of kinetic data evaluation in non-isothermal conditions are based on the well-known expression for the rate of the process:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha) = A\exp\left(-\frac{E}{RT}\right)f(\alpha) \qquad (1)$$

that can also be expressed as:

$$g(\alpha) = \int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} = \left(\frac{AE}{R\beta}\right)p\left(\frac{E}{RT}\right) \qquad (2)$$

where α is the degree of conversion, E the activation energy, A the pre-exponential factor, T the absolute temperature, R the gas constant, β the heating rate and t is the time; $f(\alpha)$ and $g(\alpha)$ are functions depending on the kinetic term model and $p(E/RT)$ is a function related with the exponential-integral resulting from the integration of the Arrhenius equation under non-isothermal (linear heating rate) conditions [6,10]. Eqs. (1) and (2) are the basic equations of, respectively, differential and integral methods for the determination of the kinetic parameters. In both cases it is assumed that the rate constant, $k(T)$, follows the Arrhenius law and parameters A and E are independent of both temperature and degree of conversion. Other prerequisites are to be considered depending on the particular method used among the numerous methods classified as differential, integral or their combinations. The advantages and drawbacks of these various methods are well documented [6,10].

Past experience has demonstrated that the determination of kinetic parameters A and E as well as of the function $f(\alpha)$ from a single DSC/DTA curve is unreliable due to the mutual dependence of the Arrhenius parameters A and E which, in turn, are affected by the choice of the model function $f(\alpha)$ [11]. As a consequence, it has been suggested [12,13] that a reliable method for the calculation of the activation energy should be used before any attempt at determining all parameters simultaneously is made.

Due to its wide applicability and reliability the Ozawa–Flynn–Wall method [14,15] is one of the most popular methods for estimating activation energy by linear heating rate thermal analysis. This method is a so-called isoconversion method type in which by using the approximation proposed by Doyle [16] for the $p(x)$ function,

$$\log p(x) \cong -2.315 + 0.4567x \quad \text{for } 20 < x < 60\left(x = \frac{E}{RT}\right) \tag{3}$$

in Eq. (2), the following linear relation can be established:

$$\log\beta + 0.4567\frac{E}{RT} = \text{constant} \tag{4}$$

Assuming that the rate constant follows the Arrhenius law and that the exothermic reaction can be considered as a single step process, the conversion at the maximum conversion rate is invariant with the heating rate when this is linear. Under these assumptions Eq. (4) is applicable to the exothermic peak maximum temperature considering different heating rates [17,18]. Thus by performing several measurements at different heating rates β_i the activation energy can be estimated directly from the slope of the graph log β_i against $1/T_{pi}$, where T_{pi} is the temperature of the DSC peak measured at a heating rate β_i, that is:

$$E \cong -2.19R\left[\frac{d(\log\beta)}{d(1/T_p)}\right] \tag{5}$$

This methodology, known as Ozawa analysis [18], is the basis of the ASTM test method E698 [19] for the estimation of the kinetic parameters of energetic materials. Once the activation energy is estimated from Eq. (5) its value can be improved by the correction of the Doyle approximation from tables provided of the correction factor $D = D(E/RT)$. Thus a new value of E can be obtained from:

$$E = -\frac{2.303R}{D}\left[\frac{d(\log\beta)}{d(1/T_p)}\right] \tag{6}$$

One of the advantages of this method is that it provides the calculation of the activation energy without any assumption concerning the model function, $f(\alpha)$. Therefore, the value of E is not conditioned by the choice of $f(\alpha)$. However, to obtain the value of the pre-exponential factor the kinetic term model must be known (see below).

The ASTM E698 also utilizes the Kissinger method [20] in which the temperature corresponding to the maximum exothermic peak is also used to compute the Arrhenius parameters. Based on several theoretical considerations, Kissinger [20] has demonstrated the validity of the relation:

$$\frac{\ln\beta}{T_p^2} + \frac{E}{RT_p} = \text{constant} \tag{7}$$

assuming that the reaction rate is maximum at the temperature T_p, at which the peak summit occurs. Thus, a plot of $\ln(\beta_i/T_{pi}^2)$ against $1/T_{pi}$ gives a straight line whose slope enables the estimation of the activation energy:

$$E = -R\left[\frac{d(\ln\beta/T_p^2)}{d(1/T_p)}\right] \tag{8}$$

The pre-exponential factor can be calculated from the maximum rate condition. This maximum rate will occur at the maximum peak temperature, T_p. Thus, considering a constant heating rate, by differentiation of Eq. (1) in order to time and after rearranging, the following equation is obtained:

$$A = -\frac{\beta E}{RT_p^2 f'(\alpha_p)}\exp\left(\frac{E}{RT_p}\right) \tag{9}$$

This implies that the form of $f(\alpha)$ should be known. In this context, the interesting work of Málek [12,13] can be mentioned, in which a method for determining the most probable expression for the kinetic model function has been developed. A straightforward procedure commonly used is to assume a first-order kinetic, that is, $f(\alpha) = (1 - \alpha)$. However, this assumption can be unacceptable in the case of solid decomposition processes if more complex mechanisms are present.

The above-mentioned methods that use exclusively the maximum peak temperatures for the determination of the Arrhenius parameters do not permit the checking of the validity of the basic assumptions in which they are based. From this point of view isoconversion methods are more reliable. Thus, Eq. (4) should be used by scanning different degrees of conversion in order to obtain several plots of log β_i against $1/T_{ij}$, where T_{ij} is now the temperature corresponding to the conversion α_j observed at a heating rate β_i. This provides a check for the invariance of E with α or, in the opposite case, for the possible complexity of the process under study.

A common requirement in all previously mentioned methods is to find a linear dependence between variables by means of a regression procedure. After estimating the regression parameters it is desirable to evaluate the adequacy of the linear model to the observed data. The index of fit most frequently used is based on the correlation coefficient. However, a large value of this coefficient does not necessarily imply that the data have been fitted well. Thus, before drawing conclusions, it is always desirable to perform statistical tests other than the simple criteria of the maximum regression coefficient. Since all sample information on lack of fit is included in the residuals, a residual analysis is a must [21]. In fact, an essential part of any regression analysis should include a careful examination of the residuals to ensure that the assumptions of the least squares theory are not violated. Ignoring this may result in biased regression coefficients, thereby leading to erroneous conclusions. This kind of treatment has been somewhat neglected in thermal analysis practice.

3. Experimental

3.1. Sample preparation

The prepared powdered samples of DNAM, with a mean particle size diameter (d_{50}) of 2.5 μm, were obtained from the same batch in which DNAM was synthesized and purified according to a procedure described elsewhere [2]. The purity of DNAM was evaluated by means of elemental analysis and the following results were obtained: Calculated (%) for $C_3H_3N_7O_5$: C = 16.58; H = 1.39; N = 45.16. Found (%): C = 16.31, 16.45; H = 1.51, 1.45; N = 45.10, 45.05.

3.2. Thermal analysis instruments, conditions and procedures

Simultaneous thermal analysis (heat flux DSC and TGA) was employed to investigate the thermal decomposition of DNAM in non-isothermal conditions. The measurements were carried out using a *Rheometric Scientific* STA 1500 equipment. Temperature calibration for both modules (DSC and TGA) was performed in the range 298–773 K by running melting standards such as indium, tin and lead (purity: 99.999%, according to the equipment manufacturer). The same standards were used in order to obtain calorimetric results in the DSC module. These calibrations were performed for each heating rate used in the subsequent experiments. The approximate resolution of the thermobalance was 0.5 μg.

The experimental procedure was planned to give, as much as possible, relevant information for the subsequent data treatment and to evaluate the reliability of dependencies between variables from a statistical point of view. The nominal heating rates of 2.5, 5, 10, 15 and 20 K $\min^{-1}$ (covering the temperature range from 298 K to 773 K) were employed and five measurements were performed for each heating rate by using sample sizes ranging from 1.39 to 2.90 mg. The samples were loaded into open alumina crucibles and a dry nitrogen purge flow of 50 ml $\min^{-1}$ at 0.1 MPa absolute pressure was used in all measurements.

4. Results and discussion

4.1. Thermal decomposition of DNAM

Typical DSC, TG, and DTG curves for DNAM obtained at heating rates of 2.5 K $\min^{-1}$ and 5 K $\min^{-1}$ are depicted in Figs. 1 and 2, respectively. It should be noted that the global patterns observed in Fig. 2 are also representative of the DSC, TG and DTG curves obtained for other heating rates (i.e. 10,

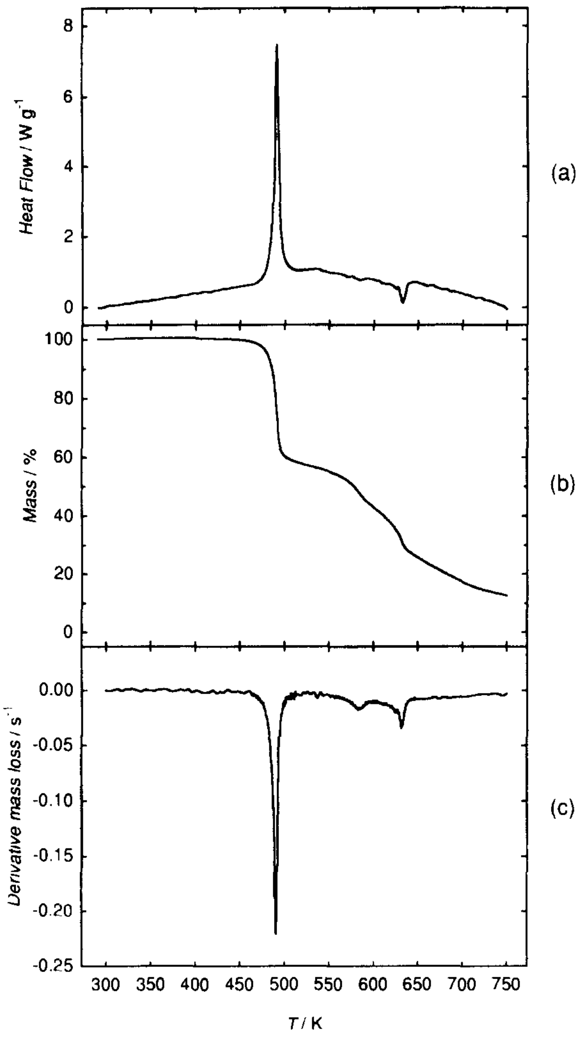

Fig. 1. (a) DSC, (b) TG and (c) DTG curves for DNAM obtained at 2.5 K min^{-1}. Sample size: 1.62 mg.

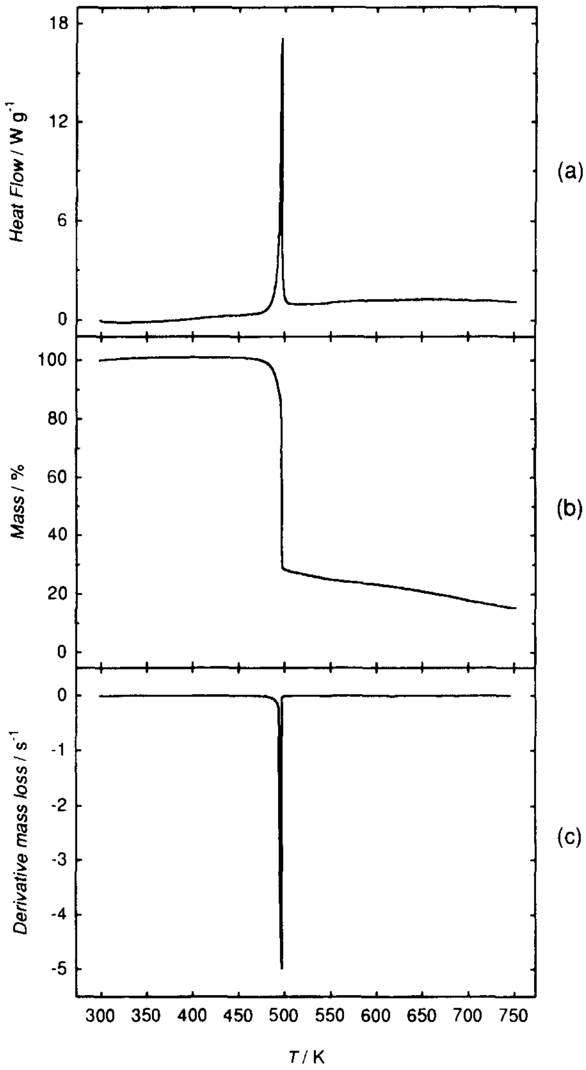

Fig. 2. (a) DSC, (b) TG and (c) DTG curves for DNAM obtained at 5 K min^{-1}. Sample size: 2.82 mg.

15 and 20 K min^{-1}). From both figures the absence of any thermal event in the temperature range below the main sharp exothermic decomposition peak can be observed. This exothermic reaction, that represents the nature of energetics of DNAM, occurs within the approximate temperature range 473–613 K considering the heating rates employed. Table 1 summarizes the peak temperatures corresponding to the DSC exothermic peaks for all runs performed. From this table it can be observed that the variability of the measured peak temperatures is acceptable and is approximately the same in all heating rates considered. The worst result was obtained for a heating rate of 15 min^{-1} with a deviation from the mean value less than 1 K. The observed differences within each group of runs carried out at each heating rate can be attributed to several factors. The uncontrollable conditions generated by the exothermic reaction itself must be considered. The sample mass and the contact between the sample and the crucible are also factors to take into account. Although great care was taken

Table 1
Exothermic peak temperatures (K) obtained in all thermal analysis measurements

Run	β/K min^{-1}				
	2.5	5	10	15	20
1	492.5	496.2	503.4	506.6	507.0
2	491.5	496.8	503.9	505.7	507.2
3	492.0	497.4	503.6	504.7	507.1
4	491.8	497.2	502.8	506.6	507.8
5	492.2	496.6	502.6	506.8	507.8
Mean	492.0 ± 0.4	496.8 ± 0.5	503.3 ± 0.5	506.1 ± 0.9	507.4 ± 0.4

while the samples were placed into the crucible, differences from run to run are to be expected.

An important characteristic that can be observed in Figs. 1 and 2 is the good stability of DNAM in a broad temperature range without any endothermic transformation (solid–solid and/or solid–liquid phase changes) prior to the exothermic reaction. Atkinson [2] has reported that 'pure dinitroammeline decomposes sharply without melting at 228°C.' This 'decomposition temperature' cannot be defined without ambiguity and even for comparative purposes common procedural factors such as the heating rate, sample size, atmosphere, among others, should be known. In this way, it can only be concluded that the decomposition temperature of DNAM reported by Atkinson [2] is within the decomposition temperature range obtained in the present study.

Considering the thermal behavior of DNAM in the whole temperature range under study, differences are noticeable when comparing the DSC, TG and DTG curves obtained for a heating rate of 2.5 K min^{-1} (Fig. 1) with the ones obtained for higher heating rates (e.g. Fig. 2). As shown in Fig. 1, the thermal decomposition of DNAM at 2.5 K min^{-1} exhibits several mass loss stages. The largest one corresponds to the exothermic decomposition process and involves a fast mass loss of 43% (43.9% ± 2.3% considering all runs performed at 2.5 K min^{-1}). After this thermal event, the mass loss of the remainder solid occurs in a variable fashion. Besides the relatively slow mass loss stages observed in the whole temperature range above 500 K, the most evident transitions that can be observed in both TG and DTG curves occur at 580 K and 630 K. The last of these transitions corresponds to the endothermic peak that is also clearly observed in the DSC curve. A distinct behavior was found for the thermal decomposition of DNAM at higher heating rates. As shown in Fig. 2, after the fast exothermic reaction, which itself involves a much higher mass loss when compared with the previous case (the observed mass losses for the heating rates 5, 10, 15 and 20 K min^{-1} were, respectively, 70.2% ± 4.1%, 69.6% ± 3.4%, 73.4% ± 6.1% and 78.8% ± 2.6%), no other kind of transformation is detectable in the DSC curve. This is also confirmed by the TG and DTG curves where after the sharp mass loss corresponding to the exothermic reaction only a very slow mass loss at approximately constant rate is observed. The differences in the variability of the mass losses during the exothermic process can also be explained, to some extent, by the above mentioned factors such as the conditions arising from the nature of the reaction, the sample mass and its placing into the crucible, among probable other less evident factors.

The global properties of the thermal decomposition of DNAM revealed by the respective thermal analysis curves do not give information about the fundamental physico-chemical processes occurring at a molecular scale. Any attempt to discuss in detail the mechanistic processes involved would be speculative in nature. Nevertheless, a global discussion based on the observed macroscopic properties can be drawn, at least on a qualitative basis.

The observed differences in the thermal decomposition of DNAM as shown in Figs. 1 and 2 suggest differences in the respective exothermic reaction mechanisms. It is well known that physical and chemical factors can have a strong influence on the decomposition mechanisms of energetic materials [22]. This topic has been also commonly discussed in thermal analysis practice [6,11]. For the case under study, the exothermic reaction can be considered of key importance because it represents the energetic nature of DNAM and the way as the exothermic reaction proceeds seems to determine the subsequent thermal processes (as can be seen by comparison of Figs. 1 and 2). In this way, it is of prime importance to discuss, as far as possible, mainly the factors that can explain the observed differences in the exothermic process. The chemical composition of the samples that were used in all measurements was virtually identical (since the samples were obtained from the same DNAM synthesis and purification procedures). Therefore, immediately before the beginning of the exothermic reaction the chemical environment within the samples would be nearly the same in all measurements and physical factors are most probably responsible for the assumed differences in the exothermic reaction mechanisms, at least in the beginning of the reaction. Since approximately the same sample mass range was covered in the five measurements performed at each heating rate and identical atmosphere conditions were used in all of them, the heating rate is itself the most probable physical factor that can explain, to some extent, the global differences in the thermal decomposition of DNAM at 2.5 K min^{-1} and at higher heating rates. Taking into account that the decomposition under consideration proceeds according to an exothermic reaction, two different regimes for this process are plausible, that is, a distinction can be made between non-ignition and ignition reactions. Slower heating rates may lead to an uniform temperature distribution within the sample at the beginning of the decomposition reaction. Under these circumstances, the rate of the heat generated by the chemical reaction will remain balanced (or quasi-balanced) throughout the exothermic process. That is, the reaction may proceed under non-ignition conditions. On the contrary, the heat supplied at higher heating rate conditions may not have time enough to be uniformly distributed throughout the sample mass during the early stages of the decomposition process which may result in a subsequent runaway and thus in a reaction under ignition conditions.

It should be realized that the heating rate can explain only partially the observed differences in the exothermic decomposition stage. Once the exothermic reaction starts, the physico-chemical environments within the reactive sample changes dramatically. The new conditions typically involve complex interactions of chemical kinetic processes with heat and mass transport processes that are very difficult to identify quantitatively [23], and the procedural factors, such as the imposed heating rate, are no longer sufficient to explain the possible differences in the reaction mechanisms. It is possible that slower heating rates cause slower energy release rates by the exothermic reaction itself which, in turn, cannot be high enough to cause the cleavage of some chemical bonds of DNAM molecule. DNAM is a nitrated derivative of melamine in which the nitramine groups, $N–NO_2$, are bound to the carbon atoms of the *s*-triazine ring. Several works on the decomposition of nitramines [22–24] have shown the importance of the nitramine group in the early stages of the decomposition process. The $N–NO_2$ bond is prone to be broken in the early decomposition stages, leading to the formation of NO_2 and other molecular and/or radical species depending on the temperature and the chemical structure of the reactant molecule [22,24]. The formation of NO_2 is of crucial importance since, if no other external oxygen source is available, it is the main oxidizer agent for the subsequent reaction steps. Considering the observed results of the thermal decomposition of DNAM, it is possible that a heating rate of 2.5 K min^{-1} was insufficient to cause the formation of the earlier reactive species such as NO_2 in a high enough rate to sustain the subsequent exothermic decomposition process in a way comparable to the one attained at higher heating rates. Therefore, depending on the heating rate, differences in the mechanisms of the overall exothermic reaction at 2.5 K min^{-1} and higher heating rates are plausible. Different reaction mechanisms can lead to different reaction products and this can explain the observed differences in the thermal behavior of the solid products subsequent to the exothermic process. It has been reported [25] that the *s*-triazine ring of melamine is highly resistant to cleavage. The pyrolysis of melamine under certain conditions can result in the formation of various cyclic azines (fused *s*-triazine rings) and some of these melamine-like compounds are reported to be stable up to temperatures above 1000 K [25,26]. It is possible that the exothermic stage of the thermal decomposition of DNAM also leads to the formation of some melamine-like compounds. In particular, for the measurements at 2.5 K min^{-1} the endothermic peak in Fig. 1 occurs, with a correspondent mass loss, at 630 K. This temperature is close to the melting temperature of melamine that occurs with decomposition at 623 K [25].

For any further detailed discussion of this subject chemical analysis of the gases as well as of the solid whose formation occurs during the exothermic stage is necessary. This is outside the scope of this work.

From the previous discussion it can be anticipated that the determination of the kinetic parameters concerning the exothermic decomposition of DNAM must be considered critically.

4.2. Determination of kinetic parameters

The activation energy was determined by using both the ASTM E698 (Eqs. (6) and (8)) and the Ozawa–Flynn–Wall (Eq. (4)) applied at various α values followed by the correction of the E value according to Eq. (6) methods. In a strictly statistical sense, the significance of the regression results depends mainly on the size of the data set. That is, in larger data sets, even small relations between variables can be significant, whereas in very small data sets, even very large relations may not be significant. From this point of view, instead of choosing 'the best' set of data that would lead to higher correlation coefficients it is desirable, as it was done, to include in each regression procedure all experimental data.

It should be noted that after checking the programmed heating rates (by running empty crucibles) an increasing deviation of the actual heating rate with the increase of its programmed values was observed. The real values, that have been employed in all calculations, were 2.5, 5.1, 10.5, 16 and 22 K min^{-1}.

As stated previously, depending on the heating rate, two different global exothermic decompositions are plausible. According to this, two different situations were considered in the application of the Eqs. (6),(8) and (4): Case I – the regression lines were determined considering all heating rates; Case II – the regression lines were determined without taking into account the subset of data corresponding to a heating rate of 2.5 K min^{-1}. Table 2 summarizes the values of the activation energy that were obtained by the Ozawa [18] and Kissinger [20] methods and by the Ozawa–Flynn–Wall [14,15] isoconversion method. The

Table 2
Estimates of the Arrhenius parameters for the exothermic decomposition of DNAM

Method	α	Case I			Case II		
		E/kJ mol^{-1}	Correlation coefficient	log(A /s^{-1})	E/kJ mol^{-1}	Correlation coefficient	log(A/s^{-1})
Ozawa [18]		269 ± 7	0.9925	26.4	266 ± 12	0.9814	25.9
Kissinger [20]		269 ± 7	0.9920	26.4	265 ± 13	0.9803	25.9
Ozawa–Flynn–Wall [14,15]	0.1	177 ± 4	0.9954		199 ± 3	0.9973	
	0.2	195 ± 8	0.9818		253 ± 10	0.9852	
	0.3	213 ± 8	0.9853		264 ± 11	0.9853	
	0.4	227 ± 7	0.9897		261 ± 11	0.9843	
	0.5	239 ± 6	0.9922		259 ± 11	0.9843	
	0.6	250 ± 6	0.9939		258 ± 11	0.9854	
	0.7	260 ± 6	0.9945		255 ± 10	0.9865	
	0.8	270 ± 7	0.9930		249 ± 9	0.9875	
	0.9	294 ± 14	0.9754		242 ± 9	0.9888	

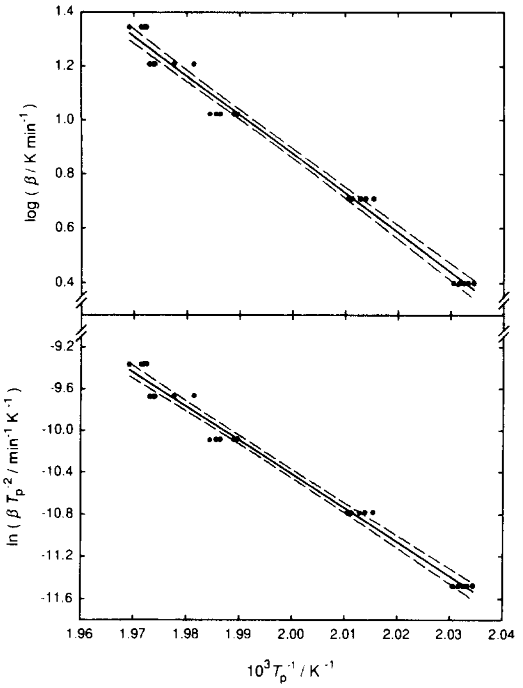

Fig. 3. ASTM analysis for Case I: (a) Ozawa method; (b) Kissinger method. (Dashed lines correspond to the 95% confidence interval around the regression line.)

degree of conversion values for this latter method were determined from the TG curves in the temperature range 473–613 K within which the exothermic reaction appeared to be completed for all heating rates employed. The pre-exponential values that are also presented were calculated by using Eq. (9) assuming a first-order kinetic.

It can be seen that both methods that are based on the measured maximum peak temperatures, whose correspondent plots (for Case I) are shown in Fig. 3, have led to the same values of the Arrhenius parameters. Furthermore, the activation energy values have not been strongly influenced by the exclusion of the subset of data corresponding to the slowest heating rate. The differences in the pre-exponential values between Case I and Case II are obviously a consequence of the kinetic compensation effect. The results obtained from the isoconversion method are quite different and Fig. 4 shows graphically the variation of the activation energy with the degree of conversion encountered for both Case I and Case II.

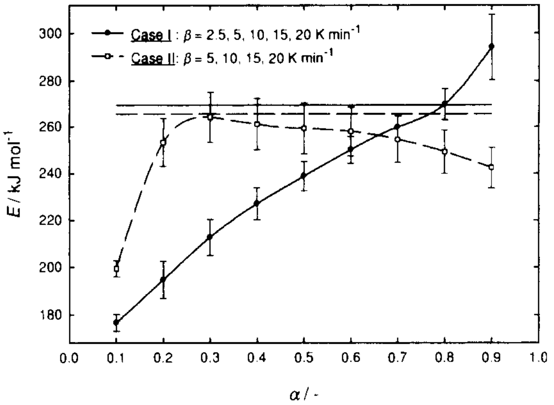

Fig. 4. Activation energy as a function of the degree of conversion calculated from the Ozawa–Flynn–Wall method.(The horizontal lines correspond to the activation energy values determined from the ASTM analysis.)

Before proceeding with any further discussion about the estimated regression parameters and thus about the activation energy values, it is imperative to check the adequacy of each linear model. For diagnostic purposes concerning the assumptions that are inherent to the linear least squares (the usual assumptions are that the errors are independent, have a zero mean, a constant variance and follow a normal distribution [21]) all sets of data were submitted to a careful statistical analysis. The statistical significance of all results was based on a 95% confidence interval.

The precision of the estimated regressions can be evaluated by performing various statistical tests, such as those that are based on F, t or χ^2 distributions. However, since these tests, even leading to statistically significant results, do not secure that the data have been well fitted, all regression procedures were also submitted to a careful residual analysis. For simplicity, only the residual analysis corresponding to the regression of log β against $1/T_p$ (Ozawa analysis) for Case I will be summarised. In all other cases the same strategy was adopted and similar conclusions were found.

In order to detect possible anomalies (that can result in biased regression coefficients), the residuals can be plotted in various ways (see Appendix A). The most usual plots are [21]: the residuals against the predicted values (Fig. 5(a)); the residuals against the predictor variable (Fig. 5(b)); and the expected normal values against the residuals (Fig. 5(c)). From both Fig. 5(a)

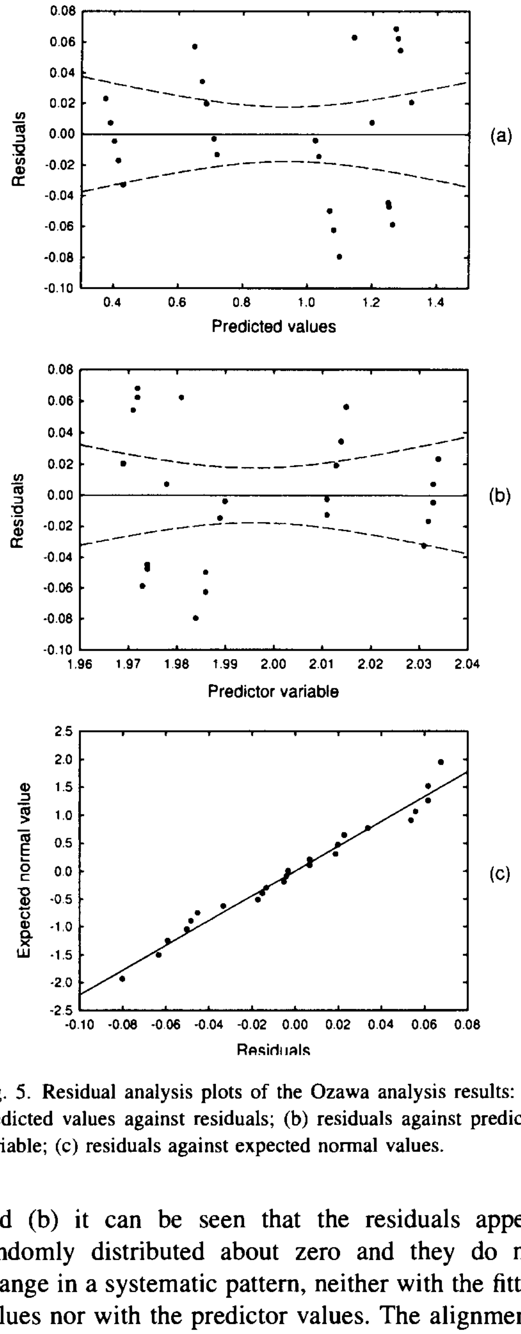

Fig. 5. Residual analysis plots of the Ozawa analysis results: (a) predicted values against residuals; (b) residuals against predictor variable; (c) residuals against expected normal values.

and (b) it can be seen that the residuals appear randomly distributed about zero and they do not change in a systematic pattern, neither with the fitted values nor with the predictor values. The alignments of subsets of data points obviously correspond to the repeated runs performed for each heating rate and should not be considered as any particular dependence in the overall residual plots. Fig. 5(c) permits confirmation that the assumption of normality was not violated since the observed residuals fall into a straight line corresponding to the normal probability plot.

The possible existence of outliers was also checked by searching for cases falling outside of ±2 times the standard deviation of the residuals. In all data analyzed it was found only one outlier, corresponding to the regression for $\alpha = 0.1$ in the isoconversion analysis for Case I. The regression analysis was then repeated with and without that outlier and it was concluded that the regression was not significantly affected by its value.

The statistical approach has shown that the assumption of the linear model was valid. Therefore, strictly speaking from this point of view, it can be concluded that the regression parameters, and consequently the activation energy values in particular, have not been distorted by the regression procedures, whatever the case considered. The precision of the activation energy values was also justly quantified. Despite the relevance of this conclusion, it does not warrant the accuracy of the obtained activation energies from the physical point of view. Indeed, there are other critical factors influencing the reliability of the kinetic analysis results to be considered.

The care that should be taken in drawing final conclusions stems from the fact that the reaction under consideration may be complex in nature. Additional difficulties arise, namely, from the heat transfer phenomena taking place throughout the process.

The obtained results, according to which differences in the activation energy values are noticeable, should be analyzed carefully. Therefore it is of interest to get an insight into the linear dependencies that have been established from the isoconversion analysis whose results are summarised in Table 2 and Fig. 4. Such linear dependencies are represented in Fig. 6 where it is interesting to compare the trends corresponding to both Case I and Case II when the degree of conversion varies. At low degrees of conversion ($\alpha = 0.1$), although the differences between the Case I and Case II are not substantial, a slight separation between the correspondent regression lines is observed. This fact can reveal that the process is susceptible of being influenced by the heating rate at the very beginning of the decomposition. Taking a look at the results at $\alpha = 0.2$ the separation between the regression lines is then further evident and a similar pattern is observed in the approximate degree of conversion range 0.2–0.4. Probably, this is a result of different reaction paths starting somewhere at the

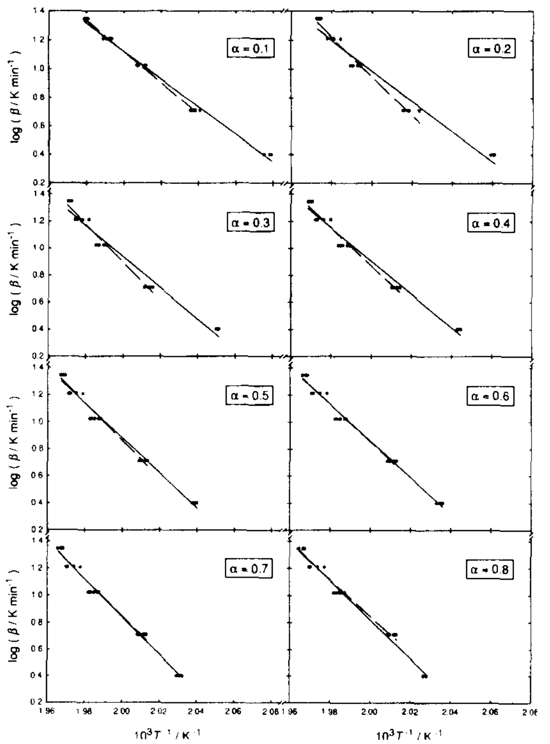

Fig. 6. Regression plots for the Ozawa–Flynn–Wall analysis. (Dashed lines correspond to Case II.)

very early stage of the decomposition during which the heating rate should play an important rule. As the decomposition reaction proceeds the influence of the heating rate seems to vanish, probably due to the new conditions generated by the chemical reaction according to which the reactive medium has changed from a heat sink to a heat source. This can explain the overlapping of the regression lines at $\alpha = 0.6$ and $\alpha = 0.7$ followed by a new separation at $\alpha = 0.8$ but now in an opposite way when compared with the observed reactions at low degrees of conversion.

These results substantiate the previously stated non-ignition and ignition conditions corresponding to the exothermic decomposition at 2.5 K min^{-1} and higher heating rates, respectively. That is, depending on the heating rate the exothermic process proceeds according to either a non-ignition regime or an ignition regime, leading to correspondingly different reaction mechanisms. In the light of this conclusion the question of the adequacy of the kinetic analysis methods employed should be raised . (Ideally, the answer to this question should be known *a priori* but this would be difficult or even impossible to attain).

From a theoretical standpoint, both Ozawa [18] and Kissinger [20] analyses can be considered as particular cases of the isoconversion methods. However, some observed facts exhibit a denial of the prerequisites of these methods. The application of the Ozawa–Flynn–Wall [14,15] analysis to Case I may be less acceptable since the mechanism of the exothermic process changes dramatically (from non-ignition to ignition conditions) when the heating rate is changed (from 2.5 K min^{-1} to higher heating rates). Nevertheless, this question may not be so critical during the pre-ignition conditions, that is, at degrees of conversion somewhere below 0.1. On the other hand, the isoconversion analysis for Case II clearly indicates that the global exothermic reaction cannot be described as a single step process. Consequently, at first sight the Arrhenius parameters determined from the ASTM analysis may appear to be erroneous. However, it is interesting to note that after a large variation of the activation energy with the degree of conversion that occurs at low degrees of conversion (below 0.2), the activation energy remains approximately constant throughout a considerable degree of conversion range (between approximately 0.2 and 0.8). The mean value of the activation energy in this range does not substantially differ from the value calculated from the ASTM analysis. Thus, it should be reasonable to consider this value as an apparent activation energy for the decomposition of DNAM under ignition conditions.

It should be mentioned that in order to find a more reliable value for the preexponential factor an attempt was made to find the most probable kinetic term model, $f(\alpha)$, based on the work of Málek [12,13]. Unfortunately, this attempt has failed and the most probable reason for this has been the conjugation of two interdependent factors: the complexity of the reaction and the principle of the operation of the equipment used to investigate the reaction. It was found that the DSC curves were not mathematically treatable for reliable results.

Despite the incomplete description of the real process given by the methods that have been used, its usefulness must be recognized. As stated by Sesták [6] (more than 10 years ago but still being valid) "It is obvious that criticism of present kinetic procedures for not characterizing sufficiently precisely the reality of heterogeneous processes is much easier than proposal of more suitable models." Furthermore, the possible inadequacy of mathematical modelling for describing solid-state decomposition kinetics is not the unique problem to take into account. The critical importance of the instrumental design in the kinetic analysis is well known. In a recent work, Ceipidor et al. [27] have underlined the strong influence that the heat transfer taking place into thermal analysis equipment can have in the kinetic measurements. In this context, it should be mentioned that the measurements were performed in a heat flux DSC (i.e. a quantitative DTA [6]). The assumption commonly made in thermal analysis measurements that the temperature of the sample changes with time in an uniform (linear) way is not always observed in practice. This is particularly true when exothermic decompositions producing heat faster than it can be dissipated to the surroundings are involved. In such cases a considerable deviation of the sample temperature from the linear program can be encountered leading to some difficulties in the subsequent kinetic analysis. To overcome this problem, besides the use of small sample sizes, some kind of diluent material can be used. However, in the measurements performed, it was decided not to use any kind of diluent to avoid possible additional competitive diffusion effects during the process. The maximum deviation of the sample temperature from the programmed rate was less than 4 K. This deviation has occurred mainly at higher degrees of conversion (above $\alpha = 0.8$) and thus the activation energy values calculated for this conversion level should be less reliable. Truly power-compensated DSC instruments are considered less susceptible to causing this kind of difficulties, although at the expense of losing the wealth of information given by simultaneous thermal analysis.

5. Conclusions

The thermal decomposition of DNAM under non-isothermal conditions by simultaneous thermal analysis has revealed a thermally stable substance in a wide temperature range below its exothermic decomposition that occurs, according to the heating rate range covered, above 473 K. No other thermal events were observed in the temperature range prior to the exothermic process. It was found that among the procedural factors the heating rate can play an important rule during the early stages of the exothermic decomposition process. This can proceed either according to non-ignition or ignition regimes and correspondingly different reaction mechanisms are therefore plausible. An attempt was made to give a global picture concerning the kinetic analysis of the exothermic decomposition process. The obtained results have substantiated the observed thermal behavior of the exothermic process being possible to consider them as an important preliminary quantitative information on the kinetics of the exothermic decomposition of DNAM.

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Appendix A

Considering that a functional dependence $y = f(x)$ can be expressed approximately by a linear relation, the following regression model can be used [21,28]:

$$y_i = B_0 + B_1 x_i + \varepsilon_i, \qquad i = 1 \ldots n \qquad \text{(A.1)}$$

where:

- y is the dependent variable, a term indicating a mathematical or statistical dependence of a variable on one (or more) other variable(s);
- x is the independent or predictor variable, a term indicating a variable that can either be set to a desired value or else take values that can be observed but not controlled;
- B_0 and B_1 are the model regression parameters, a term used to denote an unknown quantity whose values are estimated to get the best possible fit for given data;
- n is the number of observations;
- ε_i are the residuals defined as the differences $\varepsilon_i = y_i - \hat{y}_i$ $(i = 1 \ldots n)$, where y_i is an observation and $\hat{y}_i$ is the corresponding fitted or predicted

value, obtained by using the fitted regression equation.

The unknown parameters B_0 and B_1 are estimated by the method of least squares, which involves minimizing the sum of the square of the residuals:

$$S(B_0,B_1) = \sum_{i=1}^{n} \varepsilon_i^2 = \sum_{i=1}^{n} (y_i - B_0 - B_1 x_i)^2 \tag{A.2}$$

By differentiation of Eq. (A.2) with respect to B_0 and B_1, and by setting the results equal to zero, the values of B_0 and B_1 that minimize $S(B_0,B_1)$ can be obtained by solving the set of equations:

$$\sum_{i=1}^{n} (y_i - B_0 - B_1 x_i) = 0 \tag{A.3}$$

$$\sum_{i=1}^{n} x_i(y_i - B_0 - B_1 x_i) = 0$$

Thus, the following predictive equation can be obtained:

$$\hat{y} = b_0 + b_1 x \tag{A.4}$$

where $\hat{y}$ denotes the predicted value of y for a given x, and where b_0 and b_1 are the estimates of B_0 and B_1, respectively.

The least squares method is based, among others, on the assumptions that the errors (residuals) are independent, have a zero mean, a constant variance and follow a normal distribution [21]. In order to validate these assumptions and thus for detecting model deficiencies in the regression analysis, an examination of the residuals should be made. Although the residuals can be plotted in various ways, the most common plots for general diagnostic purposes are those in which the residuals are plotted against both the predicted values and the predictor variable, and the plot of the expected normal values against the residuals [21].

Both plots of the residuals against the predicted values (Fig. 5(a)) and the residuals against the predictor variable (Fig. 5(b)) are very useful for testing departures from the model assumptions. If the residuals appear randomly distributed around the centre line, then the relationship between the independent and the dependent variables is linear in nature. Otherwise, a dependence of the residuals on the predicted values and on the predictor variable according to some peculiar pattern suggests either an inconstancy of error variance or that more terms in the model are necessary.

The normal probability plot (Fig. 5(c)) provides a simple and effective method for checking to what extent the pattern of the residuals follows a normal distribution. In the ideal case the residuals will fall within a straight line when they are plotted against its expected normal value.

In short, the purpose of all these plots is to identify outliers. An outlier among the residuals is an atypical observation that can have a strong influence on the regression line and consequently on the values of the regression parameters.

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